

THERMAL ELIMINATION OF POLY(PHENYLVINYLSULFOXIDE)
AND ITS STYRENE BLOCK COPOLYMERS

BY

RUSTOM SAM KANGA

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1988



Dedicated
to
my parents
Sam and Gool Kanga

and to my mentor
the late Mr. J. Elavia

ACKNOWLEDGMENTS

I wish to thank all the members of my supervisory committee: Dr. George Butler, Dr. Kenneth Wagener, Dr. Merle Battiste, Dr. Russel Drago, Dr. Christopher Batich and Dr. James Boncella.

Special thanks are given to Dr. Batich for his help and advice in XPS, to Mr. Richard Crockett for running the XPS spectra of my polymers and to Dr. King for running the pyrolysis-MS.

I thank Dr. Wagener for his support, encouragement and sagacious advice, both chemical and non-chemical.

I am gratefully indebted to Dr. Thieo Hogen-Esch for his direction, guidance, encouragement and best of all patience. He taught me a lesson I will never forget: avoid mediocrity!

Thanks are offered to Lorraine Williams for her ready smile and readier help. Thanks and cheers are expressed to all the people on the polymer floor for having enriched my existence.

Words cannot express my gratitude nor my indebtedness to Pauline Schneider for her help in preparing this manuscript and for being there at the most critical point in my life!

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENTS.....	iii
KEY TO ABBREVIATIONS.....	vii
ABSTRACT	viii
 CHAPTER	
1 INTRODUCTION.....	1
Polyacetylene (PA).....	3
Precursor Routes to Polyacetylene.....	5
2 EXPERIMENTAL.....	11
High Vacuum Anionic Polymerization Techniques.....	11
Purification of Solvents, Monomers and Reagents.....	12
Purification of Phenylvinylsulfoxide and Ethylphenylsulfoxide..	12
Purification of Styrene and 1,1-Diphenylethylene.....	13
Purification of t-Butyllithium.....	16
Preparation of Initiators.....	16
Lithium Naphthalide.....	16
Triphenylmethyllithium (TPML).....	18
1,1 Diphenylhexyllithium (DPHL).....	20
Triphenylmethylpotassium (TPMK).....	20
1-Lithio-1-(Phenylsulfinyl) Ethane (EPSL).....	20
Determination of Concentration of Carbanions.....	22
Titration with Fluorene.....	22

	Determination of Concentration by UV/Visible Spectroscopy.....	23
	Polymerization of Phenylvinylsulfoxide.....	24
	Copolymerization of Styrene and Phenylvinylsulfoxide.....	28
	A-B Copolymers.....	28
	A-B-A Triblock Copolymers.....	33
	Monomer Conversion Study.....	34
	Thermal Elimination.....	36
	Instrumental Methods.....	38
	Size Exclusion Chromatography (SEC).....	38
	Capillary Gas Chromatography (GC).....	39
	Nuclear Magnetic Resonance Spectroscopy (NMR).....	39
	Infrared Spectroscopy (IR).....	40
	UV/Visible Spectroscopy.....	41
	Polarimetry.....	41
	Pyrolysis-Mass Spectrometry.....	41
	Thermogravimetric Analysis (TGA).....	42
	X-Ray Photoelectron Spectroscopy (XPS).....	42
	Contact Angle of PPVS Homo- and Copolymers.....	44
3	HOMOPOLYMERIZATION AND COPOLYMERIZATION OF PVS.....	45
	Homopolymerization.....	45
	Initiators.....	47
	Nature of the Propagating Carbanion.....	48
	Effect of Temperature.....	52
	Effect of Temperature on Initiation of PVS.....	54
	Effect of Temperature on Polymerization.....	59
	Conversion of (\pm) PVS With Time.....	65
	Polymerization and Studies of (+)-PVS.....	67

Copolymerization of Styrene and PVS.....	67
A-B Copolymers.....	67
A-B-A Copolymers.....	76
Proof of Dianion Formation in the Lithium Naphthalide Initiated Polystyryllithium.....	79
4 THERMAL ELIMINATION STUDIES.....	85
Mechanism of Sulfoxide Elimination.....	85
Use of Sulfoxides as Acetylene Synthons.....	88
Michael Addition-Elimination.....	88
Alkylation-Elimination.....	88
Sulfenylation-Dehydrosulfenylation.....	91
Diels-Alder Cycloadditions and Elimination.....	91
1,3 Dipolar Cycloaddition and Elimination.....	91
Elimination of PPVS and PS-PPVS Copolymers.....	91
Fate of Phenyl Sulfenic Acid.....	94
Thermal Methods for Study of Elimination.....	98
Thermogravimetric Analysis (TGA).....	98
Pyrolysis-Mass Spectrometry.....	106
Studies of the Elimination of PPVS by Spectroscopic Methods	112
X-Ray Photoelectron Spectroscopy (XPS).....	112
Nuclear Magnetic Resonance (NMR).....	116
Infrared (IR).....	125
REFERENCES.....	129
BIOGRAPHICAL SKETCH.....	135

KEY TO ABBREVIATIONS

PVS.....	phenylvinylsulfoxide
PPVS.....	poly(phenylvinylsulfoxide)
PPVO.....	poly(phenylvinylsulfone)
PA.....	polyacetylene
PS.....	polystyrene
EPS.....	ethylphenylsulfoxide
TPML.....	triphenylmethyllithium
1,1-DPE.....	1,1-diphenylethylene
GC.....	gas chromatography
SEC.....	size exclusion chromatography
MW.....	molecular weight
M _n	number average molecular weight
M _w	weight average molecular weight
M _p	peak molecular weight from SEC
XPS.....	X-ray photoelectron spectroscopy

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

THERMAL ELIMINATION OF POLY(PHENYLVINYLSULFOXIDE)
AND ITS STYRENE BLOCK COPOLYMERS

By

Rustom Sam Kanga

December 1988

Chairman: Dr. Thieo E. Hogen-Esch
Major Department: Chemistry

The polymerization of phenyl vinyl sulfoxide (PVS) was carried out in THF at -78°C using various anionic initiators. It was found that delocalized carbanion initiators such as triphenylmethyllithium are effective initiators as are methyllithium and the dipole stabilized 1-lithio-1-(phenylsulfinyl) ethane. There was excellent correlation between the measured molecular weight and the calculated molecular weight. The molecular weight distribution was found to be narrow (≤ 1.4). The polymerization reaction was found to be extremely rapid with a half life time of about 4 seconds. A side reaction at higher temperatures was observed leading to broadening of the molecular weight distribution. The effect of counter ion, solvent polarity and temperature on the polymerization reaction was investigated.

Both A-B and A-B-A block copolymerization were carried out. The A-B diblock copolymerization was carried out by vapor-phase

polymerization of styrene in THF at -78°C using t-butyllithium initiator followed by capping with 1,1-diphenylethylene. The capped polystyryllithium was used for initiation of the PVS block. The A-B-A triblock copolymerization was carried out by reacting two-ended polystyrene prepared by using lithium naphthalide as initiator with 1,1-DPE to give a capped stable living dianion of polystyryllithium which initiated PVS at both ends to give an A-B-A triblock copolymer, polystyrene being the inner block. The molecular weight distributions of the block copolymers were, in general, narrower than the homopolymers.

The thermal elimination of the homo and copolymers was studied by TGA and pyrolysis-MS. The TGA of homopolymers typically show two degradation stages: one at lower temperatures corresponding to elimination of phenyl sulfenic acid and one at higher temperatures corresponding to polyacetylene degradation. Pyrolysis-MS was used for elucidating the fate of phenyl sulfenic acid formed upon elimination. XPS was used to monitor the elimination reaction with temperature. Proton NMR was also used to characterize the elimination process and shows formation of cis and trans polyenes at high temperatures ($>100^{\circ}\text{C}$). A change in IR spectra with temperature was observed but gave no useful information about the polyenes formed.

Preliminary studies carried out elsewhere show a relatively short conjugation length in the polyacetylene formed. Preliminary conductivity measurements are in progress.

CHAPTER 1 INTRODUCTION

In the course of previous investigations on the mechanism of anionic oligomerization and polymerization of phenyl vinyl sulfoxide (PVS) [1, 2] it was discovered that poly(phenylvinylsulfoxide) (PPVS) upon standing, either in the solution or the solid state, at room temperature changed color from white to yellow within 24 hours. The polymer then became red and finally black within one week. The color change occurred in dark or in the presence of light. It occurred in air, under vacuum or under an argon atmosphere. The color change, indicating decomposition of some type, was suppressed to some extent by storage at freezer temperatures.

These color changes were also observed while warming in a melting point apparatus and were essentially immediate upon heating the polymer above 100-150°C. Interestingly when PPVS was oxidized to poly(phenylvinylsulfone) the above color changes were not observed upon heating. The color changes were consistent with the formation of polyacetylene through a concerted, cyclic, sigmatropic thermal elimination of phenyl sulfenic acid from PPVS illustrated in Figure 1-1. The sulfoxide elimination was first proposed by Kingsbury and Cram [3] and later used as an acetylene equivalent in a Michael addition-elimination [4-9], and a Diels-Alder cycloaddition-elimination [10] for introduction of a vinyl group in organic syntheses. Thus PPVS could be regarded as a soluble polyacetylene precursor.

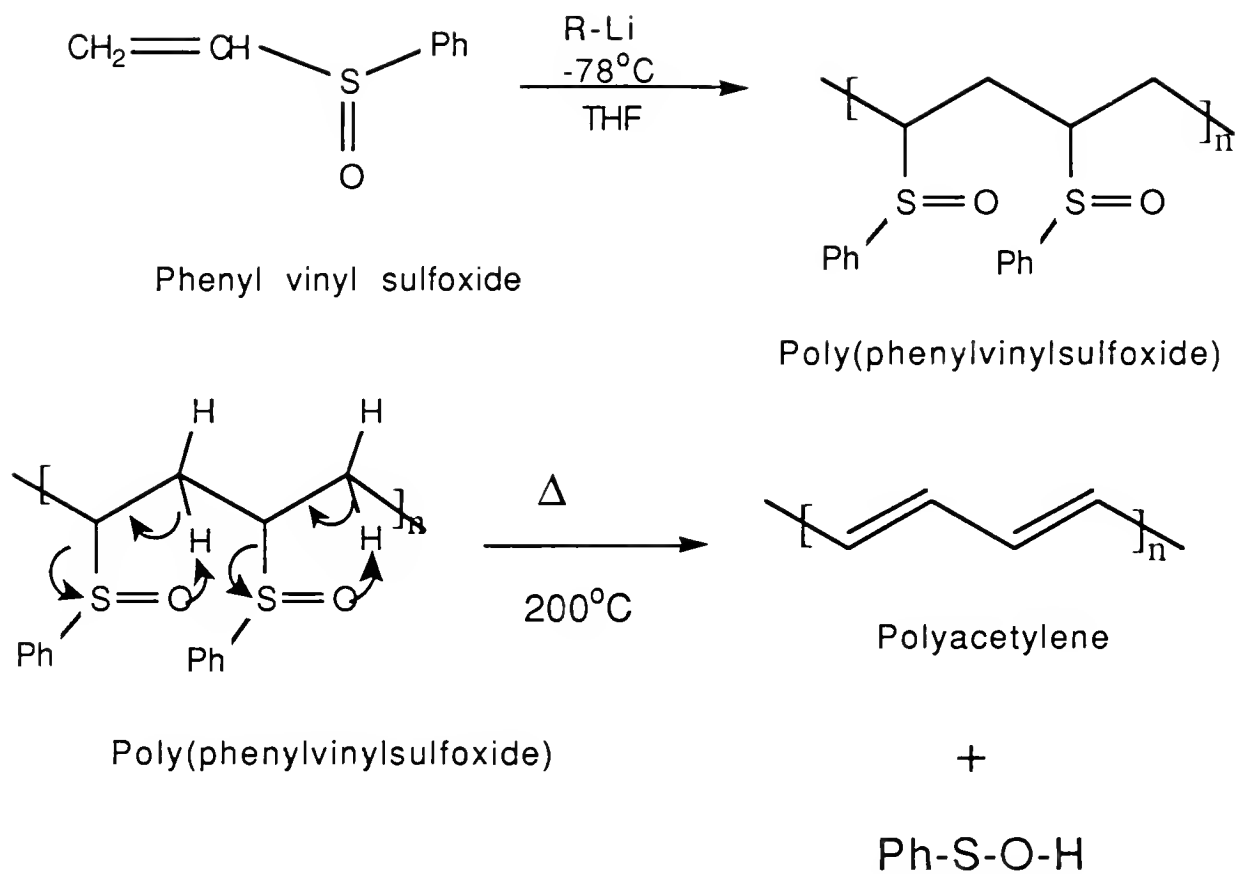


Figure 1-1. Scheme for the elimination of phenyl sulfenic acid from PPVS.

Polyacetylene (PA)

Polymers with conjugated π -electron backbones are currently of intense research interest worldwide [11-20]. This is because this class of polymers displays unusual electronic properties such as low energy optical transitions and low ionization potentials. As a result they can be oxidized or reduced more readily and reversibly than conventional polymers without conjugation [11]. Therefore an insulating polymer could be converted into conducting polymers with near metallic conductivity in many cases. Polyacetylene, the simplest conjugated polymer has become a prototype in the conducting polymers field and has been the most widely studied of the conducting polymers.

The main impetus for the study of conducting polymers was provided when Shirakawa [12] successfully synthesized PA as a coherent free standing film. They used an unusually high concentration of a Ziegler-type catalyst system. When acetylene gas was introduced into a vessel containing $\text{Ti}(\text{OC}_4\text{H}_9)_4$ / $\text{Al}(\text{C}_2\text{H}_5)_3$ (Al:Ti::4:1) in toluene (0.1-0.2 M in Ti) at -78°C , a lustrous film formed at the gas-liquid surface. This polymer referred as "Shirakawa polyacetylene" had a lustrous, golden appearance and predominantly cis-geometry and was an insulator. The cis-PA isomerized to trans at higher temperatures ($>150^\circ\text{C}$) or upon doping with electron acceptors such as iodine or AsF_5 (called p-doping) or with electron donors like sodium or potassium naphthalide (called n-doping). In the pristine form cis-PA is an insulator ($\sigma = 10^{-9}$ S/cm) whereas trans-PA is a semi-conductor ($\sigma = 10^{-5}$ S/cm). Upon doping, however, conductivities as high as 10^3 have been obtained [13]. Recently Naarman in W. Germany [14] report an improved synthesis of PA with fewer SP_3 defects having conductivity in the range of 1.5×10^5 which is about one-fourth the

conductivity of copper by volume and twice the conductivity of copper by weight!

The doping of conjugated polymers results in high conductivities primarily by increasing the carrier concentration. The description of this process as doping is a misnomer since dopant concentrations are exceptionally high compared to the conventional doping of inorganic semiconductors. In some cases the dopant constitutes about 50% of the final weight of the conducting polymer [11]. Thus the system would be more appropriately described as a conducting charge-transfer complex rather than a doped polymer. Conductivity in doped polymers may be due to electron transport through the chain (intramolecular), between chains (interchain transport) and also through interparticle contact [11].

PA is an inconvenient material for fabrication. It is insoluble in all solvents and cannot be melt processed. Intractability is the major hurdle for large scale commercial application of PA. Also PA as synthesized can undergo oxidation in air fairly readily resulting in a severe drop in conductivity [13].

Another problem is contamination of the PA sample with catalyst residues which may influence the detailed outcome of the individual measurements of conductivities which varies with the details of preparation, recovery, and the washing technique. PA has a fibrillar mat morphology in which only one third of the space available is occupied by the PA fibrils. Generation of alternate morphologies has resulted in little success. The necessity of producing the film at the interface between a catalyst solution and acetylene gas limits the physical form in which PA can be produced and this restricts the utility and applicability of direct synthesis. Considerations of this kind lead to the conclusion that a two

step precursor route to synthesis of PA would be advantageous in circumventing one or more of the above problems. Thus a soluble precursor could be generated which on further chemical reaction would yield PA in the second step.

Precursor Routes to Polyacetylene

Precursor routes to PA are not unknown [16-20]. Marvel et al. were the first to consider dehydrohalogenation of polyvinylhalides to form PA [15]. Unfortunately they found that under the extreme reaction conditions used (high temperatures in presence of high local concentrations of HX) the nascent polyene formed undergoes further reactions.

Precursor routes for PA syntheses have been extensively studied by Feast in Durham, U.K. Their approach is outlined in Figure 1-2 and 1-3. The precursor polymers are synthesized by a metathesis ring-opening polymerization of monomers like 7,8-bis(trifluoromethyl) tricyclo {4.2.2.0^{2,5}} deca-3,7,9-triene (Figure 1-2) [17, 18]. These precursor polymers are obtained as colorless soluble materials by conventional reprecipitation and films or fibres could be spun from solution. A 1,2-disubstituted benzene is thermally eliminated from the precursor polymer in a symmetry allowed step to yield PA. Cis-PA is initially formed which isomerizes to trans-PA at higher temperatures. Under increasingly applied stress ordered films of PA can be produced. This two step approach allows a whole range of new morphologies to be prepared and investigated [16,17].

Recently Grubbs [20] found that ring opening metathesis polymerization (ROMP) of benzvalene yields poly(benzvalene) which is a polyacetylene precursor. ROMP of benzvalene was achieved using well-defined non-Lewis acid tungsten alkylidene metathesis catalysts like

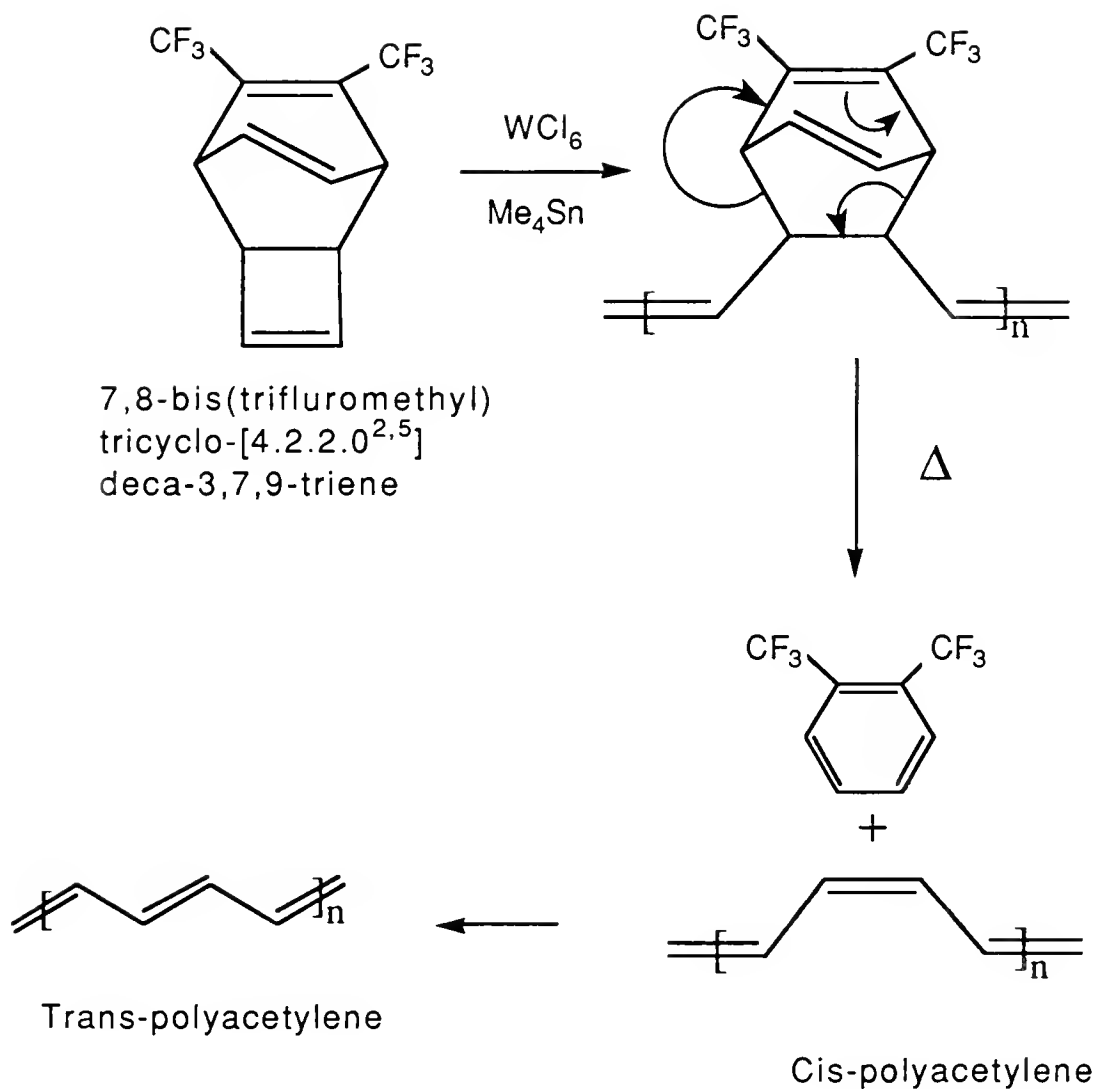


Figure 1-2. Precursor route -1- to "Durham Polyacetylene."

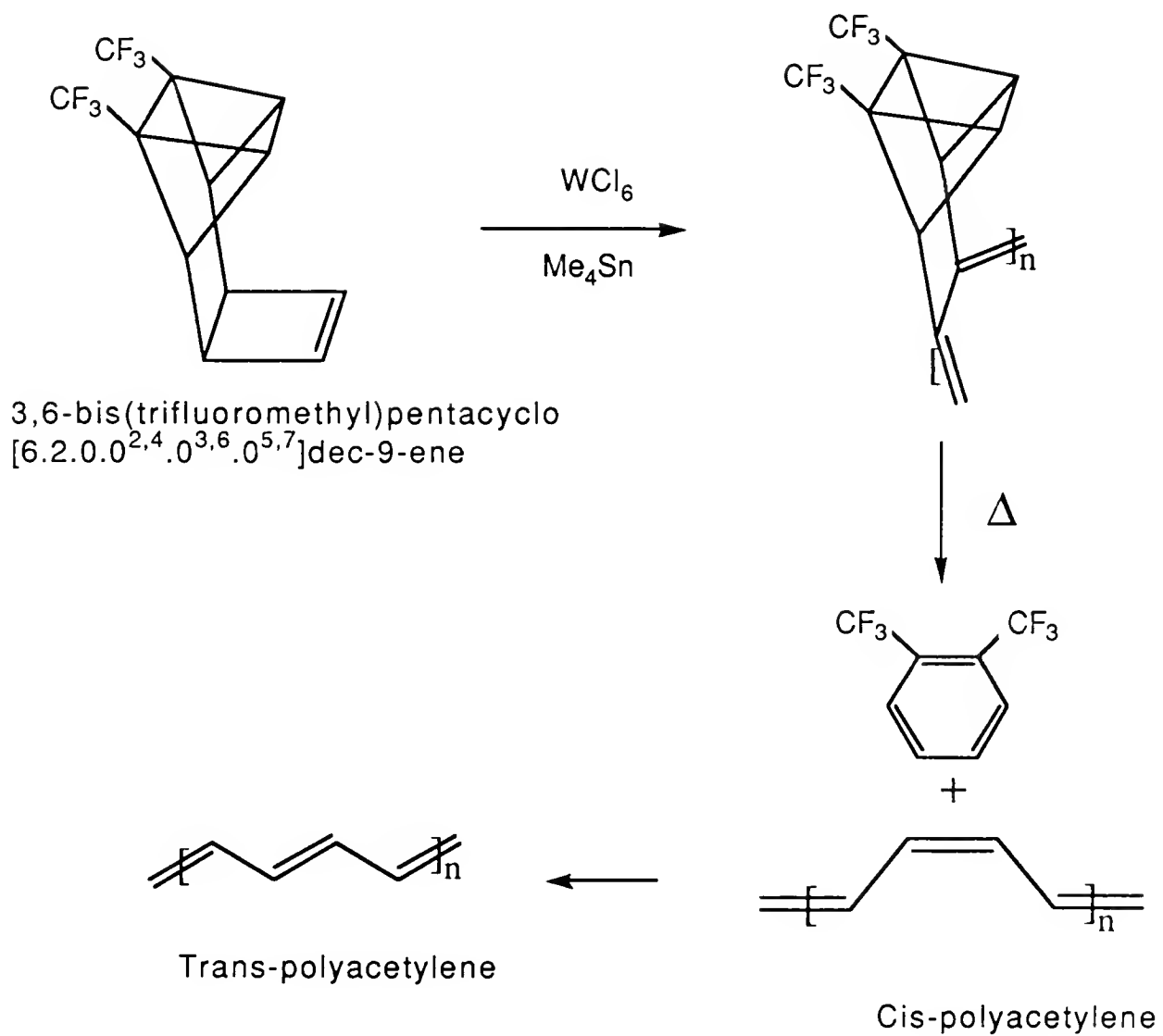


Figure 1-3. Precursor route -2- to "Durham polyacetylene."

Schrock's catalyst $\{(RO)_2W(N(2,6-(iPr)_2Ph))CHC(Me)_3\}$ [Figure 1-4].

Poly(benzvalene) isomerizes to PA by the action of transition metal catalysts like $HgCl_2$, $HgBr_2$, and Ag^+ salts in THF. The thermal and photochemical isomerizations were unsuccessful.

The SEC studies of poly(benzvalene) reveals a very broad molecular weight distribution ranging from 1000 to 600,000 with average molecular weight approximately 20,000 (relative to polystyrene standards). The conductivities of the doped PA was 1 S/Cm [20] which was comparable to Durham PA but is much lower than Shirakawa and Narmann PAs. This may be due to the amorphous morphology formed during the isomerization.

The synthesis of PA from PPVS in our case has potential advantages. Firstly the polymerizations of PVS proceeds through stable carbanions (Chapter 3) so that the molecular weight distribution is expected to be narrow (unlike those of the Durham and Grubb precursors). Moreover the control of molecular weight through the ratio of monomer to initiator is quite good and thus formation of high molecular weight PPVS is possible. As a result a series of monodisperse PAs of known molecular weights is possible. Unlike the previous precursor routes which use exotic and difficult chemistry, the anionic polymerization of PVS is simple and uses readily available reagents and well-known techniques.

A second advantage of the sulfoxide precursor route to PA is the formation of A-B and A-B-A type copolymers with monomers like styrene, butadiene, isoprene etc which are accessible through living anionic polymerizations. These may then be subjected to elimination to form block copolymers of styrene (or other monomers) and PA. Previous attempts to make block copolymers of PA have been known [21-24]. There have been two different approaches to make PA block copolymers. Aldissi [21-22]

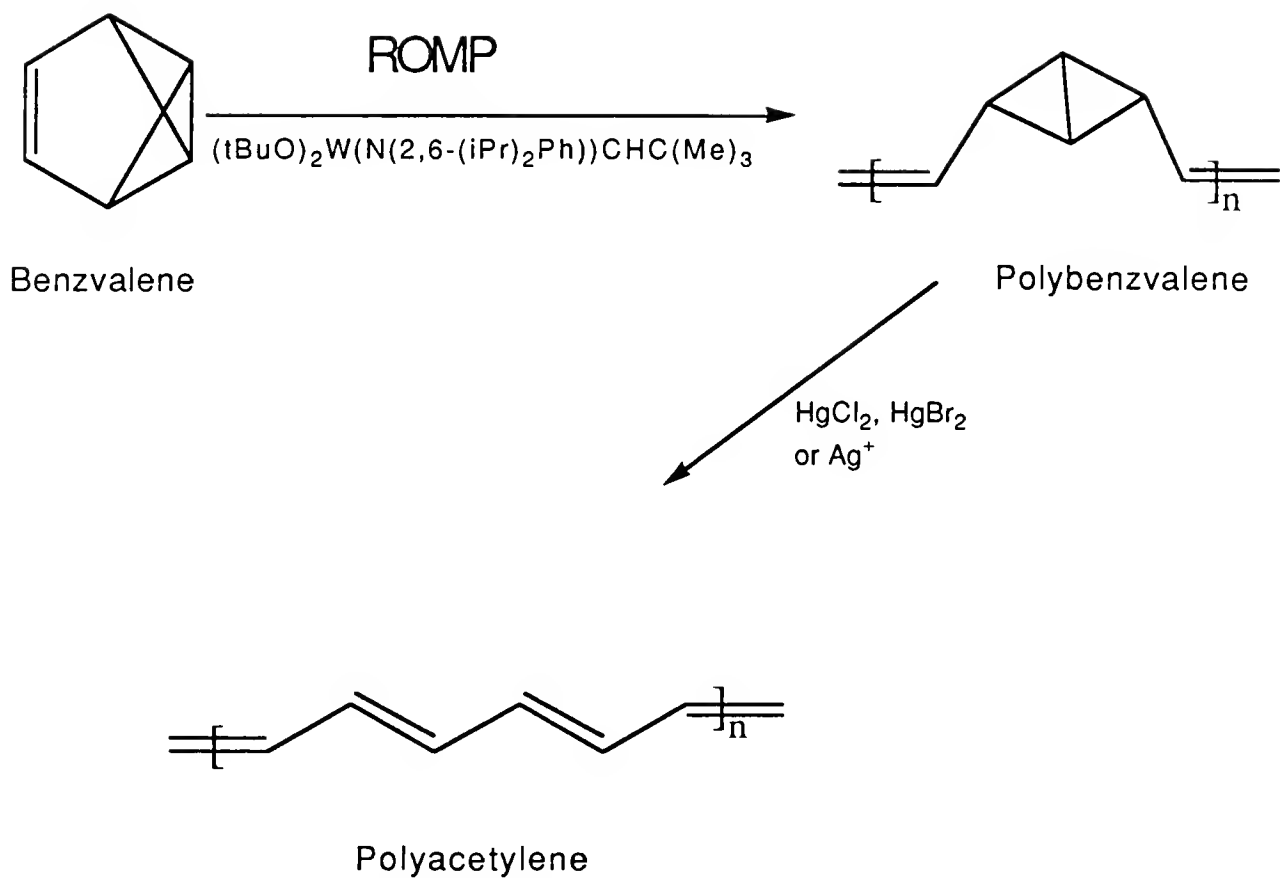


Figure 1-4. Ring opening metathesis polymerization of benzvalene to polybenzvalene, a polyacetylene precursor.

had proposed an "anionic to Ziegler-Natta catalyst" approach wherein the styrene, isoprene etc have been polymerized anionically followed by addition to a Ziegler-Natta catalyst like $\text{Ti}(\text{OBu})_4$ which exchanges one of the ligands with the anionically growing polymer chain. Acetylene gas was then introduced to make the soluble block copolymer. Baker and Bates have used a similar approach to make both block and graft copolymers [23]. Stowell et al. [24] on the other hand used the "anionic to metathesis catalyst" approach to make block copolymers of PA. They react the growing polystyryllithium with a co-ordination catalyst like WCl_6 and polymerize acetylene with the WCl_6 /polystyryllithium catalyst. Our approach to make block copolymers would be one using the traditional anionic block copolymerization technique where styrene is first polymerized using alkyllithium initiator followed by capping with 1,1-diphenylethylene and the capped polystyryllithium would be used to polymerize PVS. The copolymer could then be subjected to thermolysis to make the poly(styrene-b-acetylene).

Thus the purpose of the present study was twofold: (i) to synthesize and characterize PVS homopolymers and its block copolymers with styrene (both A-B and A-B-A) and (ii) to demonstrate the thermal elimination of phenyl sulfenic acid from the homo- and copolymers to form PA and its block copolymers.

CHAPTER 2 EXPERIMENTAL

High Vacuum Anionic Polymerization Techniques

Anionic polymerizations are extremely sensitive to trace amounts of electrophilic impurities. Thus rigorous techniques for purification of reagents and solvents were found to be necessary. Also most of the reagents, solvent transfers, etc. were carried out under high vacuum (10^{-6} Torr).

High vacuum line techniques have been well known for decades [25,26,27] and routinely used in our group. The vacuum system consists of a rotary oil pump in conjunction with a mercury or oil diffusion pump. The vacuum line was custom made in our glass shop, constructed entirely of pyrex glass. High vacuum pyrex ground glass joints (Eck & Krebs) were used at various junctions in the line to permit evacuation of reaction vessels and distillation of solvents from one part to another. A mercury McCleod gage attached to the manifold was used to monitor the pressure in the system.

The reaction vessels used in most of the reactions were made from pyrex and were self built by use of a hand-held gas and oxygen torch. The manipulations required for various reactions like addition, transfer of reagents etc. were performed in vacuo using the breakseal technique [25,26]. The glassware used was scrupulously cleaned using in order: KOH / isopropanol (15% W/V), 1% HF, rinsed with water and acetone and dried before attaching it to the line. Once attached to the line the whole system

was evacuated and flamed thoroughly with a torch to remove traces of adsorbed water vapor and oxygen from the surface of the glass. The system was then checked for the presence of pinholes using a Tesla coil. Reactions were carried out only after confirming "sticking vacuum" ($\leq 10^{-6}$ Torr) as registered on the McCleod gage.

Purification of Solvents, Monomers and Reagents

All polymerizations and other reactions were carried out under high vacuum in THF. Since anionic polymerizations involve reactive intermediates, it was found necessary to use highly purified and dry reagents and solvents. THF was purified by refluxing over a sodium/potassium alloy for 24 hrs., followed by distillation onto fresh alloy in a round bottom flask which was then flushed with argon and connected to a vacuum line equipped with a water-jacketed condenser. A small amount of benzophenone was added as an indicator. The THF was evacuated and degassed several times. The color turned purple which indicates formation of the benzophenone dianion and absence of protic impurities and oxygen.

Purification of Phenylvinylsulfoxide and Ethylphenylsulfoxide

Phenylvinylsulfoxide (Aldrich) in the crude form is a dark brown high boiling liquid. The crude phenylvinylsulfoxide was stirred over calcium hydride for 24 hrs., followed by distillation in a Vigreux distillation apparatus at 100-110°C / 0 mm Hg onto fresh calcium hydride. This procedure was repeated thrice. The colorless distillate from the last distillation was collected in a break-seal equipped ampule and further divided as needed. Care was taken while sealing to make sure that none of the high boiling monomer remains at the site being sealed and which might degrade forming undesirable impurities.

Other purifying agents were tried but did not work. The monomer became black within minutes when stirred over potassium mirror. McGrath [28-29] has advocated the use of triethylaluminum for the purification of acrylate and methacrylate monomers. The trialkylaluminum forms a colored charge-transfer complex with the carbonyls of the monomer and hence is self-indicating in the titration. We tried using triethylaluminum once with disastrous results! There was a strong exothermic reaction between PVS and triethylaluminum and ultimately an explosion!

The monomer was characterized by GC (>99% pure) and by proton and carbon-13 NMR.

^1H NMR (CDCl_3 , 200 MHz, δ in PPM): d at 5.85 (1H), d at 6.15 (1H), d of d at 6.6-6.8 (1H), 7.45 (3H), 7.6 (2H)

^{13}C NMR (CDCl_3 , 50 MHz, δ in PPM): 121 (vinyl methylene), 125 (ortho aromatic carbons), 131.5 (para carbon), 143 (vinyl methine), 143.5 (substituted quaternary aromatic).

(+) Poly(phenylvinylsulfoxide) was synthesized by M. Buese [2]. It was purified by distilling twice over calcium hydride. The optical rotation, $[\alpha]_{\text{D}}^{20}$, was found to be 358.5°.

Ethylphenylsulfoxide (ICN Pharmaceuticals, INC.) was purified in a similar manner.

^1H NMR (CDCl_3 , 200 MHz, δ in PPM): t at 1.1 (3H), q at 2.75 (2H), m at 7.6 (5H).

^{13}C NMR (CDCl_3 , 50 MHz, δ in PPM): 10 (methyl), 52 (methylene), 126, 131, 132, 147 (aromatics).

Purification of Styrene and 1,1-Diphenylethylene

Styrene (Fisher) was purified by stirring over calcium hydride for 24 hrs. followed by fractional distillation under vacuum (75°C / 95 mm Hg).

The middle fraction was collected in an ampule. The ampule was further attached to an apparatus shown in Figure 2-1 and evacuated. The side arm contained freshly cut potassium metal which was heated gently with a torch to form a shiny mirror in the main container. Styrene was then added onto the mirror and allowed to stir gently for 30 minutes. After degassing it was distilled into the side flask provided with a break-seal and carefully sealed off from the main apparatus. The extremely pure and dry styrene was stored in the freezer and used as needed. Styrene-d8 (Aldrich) was purified by distilling twice over calcium hydride in vacuo.

Styrene: ^1H NMR (CDCl_3 , 200 MHz, δ in PPM): d at 5.11 (1H), d at 5.59 (1H), d of d at 6.59 (1H), 7-7.5 (5H)

Styrene: ^{13}C NMR (CDCl_3 , 50 MHz, δ in PPM): 113 (vinyl methylene), 126 (ortho aromatics), 127.8 (para aromatic), 128.5 (meta), 137 (vinyl methine), 138 (substituted quaternary). Styrene-d8: ^1H NMR (neat with TMS, 200 MHz, δ in PPM): t at 5.0 (1H), t at 5.5 (1H), d at 6.5 (1H), s at 7.0 (para 1H), s at 7.1 (meta 2H), s at 7.25 (ortho 2H).

^{13}C NMR (neat with 1% CDCl_3 , 50 MHz, δ in PPM): pentet at 112.5 (vinyl methylene CD_2), t at 125.6 (aromatic ortho CD), t at 126.9 (aromatic para CD), t at 127.7 (aromatic meta CD), t at 136.2 (vinyl methine CD), s at 137.1 (substituted aromatic quaternary C). All assignments made from non-deuterated styrene in Sadtler.

1,1-Diphenylethylene was purified in a similar manner. ^1H (200 MHz, CDCl_3 , δ in PPM): s at 5.4 (2H), m at 7.2 (10H)

^{13}C (50 MHz, CDCl_3 , δ in PPM): 114 ($=\text{CH}_2$), 127.5 (ortho aromatic), 128.1 (m and p aromatic), 141.5 (ipso aromatic), 150 ($>\text{C}=\text{}$).

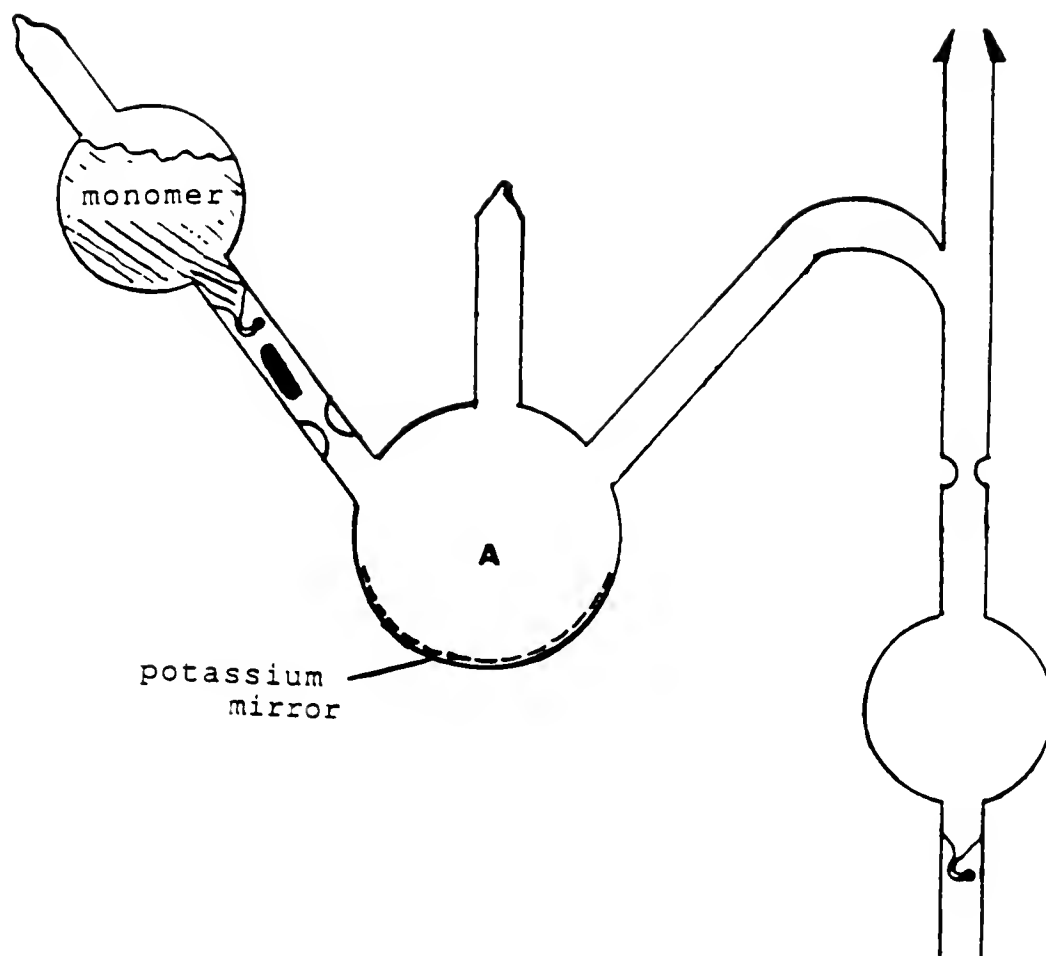


Figure 2-1. Apparatus used for purification of styrene.

Purification of t-Butyllithium

It was found that the crude t-butyllithium (Aldrich) contained undesirable impurities like lithium t-butoxide, lithium hydroxide etc. It was thus found desirable to further purify t-butyllithium by sublimation of the crude product [30]. The apparatus shown in Figure 2-2 was used.

Crude t-butyllithium was introduced in "a" under a constant flow of argon. The solvent was pumped off into the trap and the side arm sealed. Crushed dry ice was put in the cork ring on the flask "b" to trap the subliming t-butyllithium. The lower part of the apparatus was immersed in a hot water bath (85°C) and the combination of heat and dynamic vacuum was used to sublime highly pure t-butyllithium which was trapped in "b" while the impurities remained unaffected in "a." The flask containing the t-butyllithium was sealed off from "a" at the constriction "S1" and from the line at "S2." Extreme care was taken to see that none of the t-butyllithium remained at the sites "S1" and "S2" which might form undesirable decomposition products and might also create pinholes. The shiny white solid t-butyllithium was then dissolved in Na/K dried hexane and further subdivided as needed.

Preparation of Initiators

Lithium Naphthalide

Lithium wire (Mallinckrodt) was cleaned by dipping successively in methanol, hexane, and finally THF. A THF solution of naphthalene (Aldrich, Gold label) was prepared in vacuo in a break-seal equipped ampule. An excess of naphthalene was used to avoid formation of the naphthalene dianion [31, 32]. The lithium metal was introduced in the reaction vessel under a constant flow of argon. After evacuation more THF was distilled in. The naphthalene solution was then added in. A noticeable color change

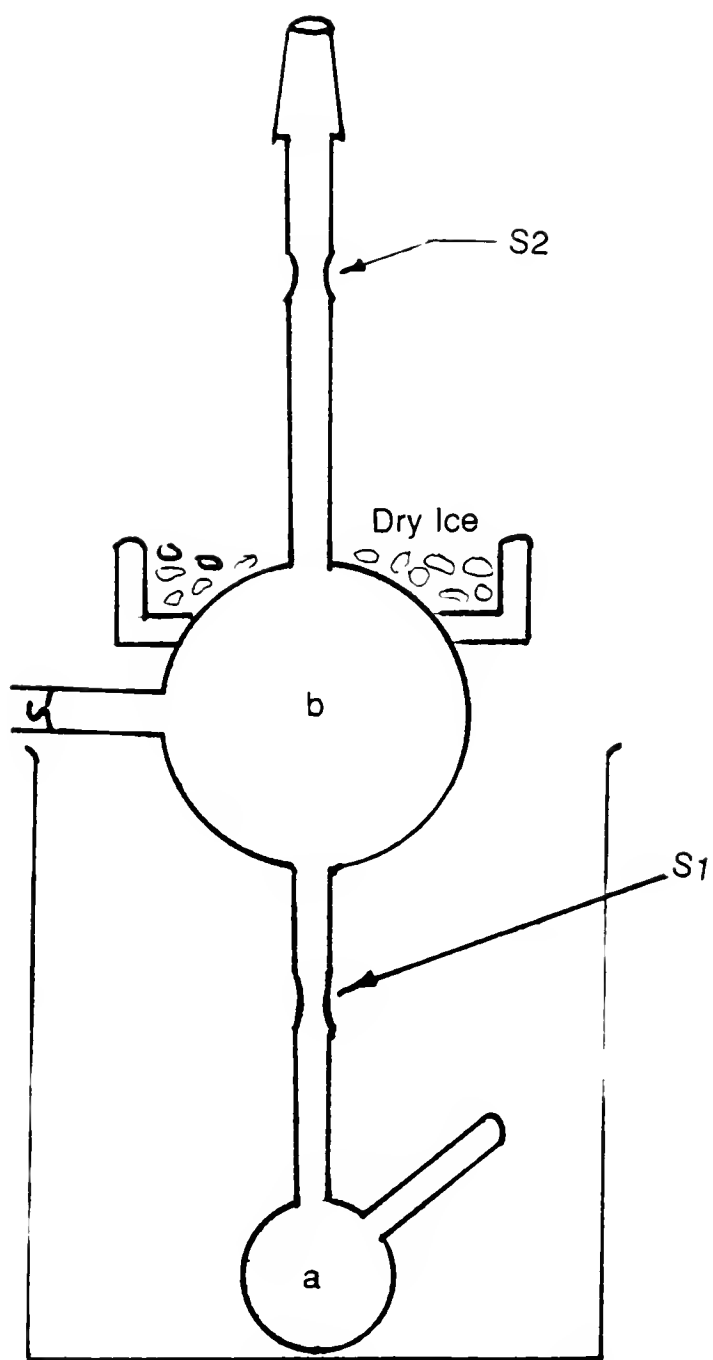


Figure 2-2. Apparatus used for purification of t-butyllithium by sublimation.

was observed upon reaction of naphthalene with lithium metal. The reaction was allowed to proceed at 25°C for 12 hrs. At the end of 12 hrs. a dark green solution was obtained which was filtered through a coarse frit into various ampules. The concentration of the initiator was determined as described later.

Triphenylmethyllithium (TPML)

TPML was made as described in reference 33. A THF solution of triphenylmethane (TPM) was prepared in vacuo and attached to an apparatus illustrated in Figure 2-3. The apparatus was attached to the line, evacuated and flame degassed. Argon was then charged into it and n-butyllithium was injected through the serum cap. Both argon and the solvent were removed by distillation into the cold trap leaving behind the viscous yellow n-butyllithium. The apparatus was cooled to -78°C using a dry ice/isopropanol bath and the serum cap was sealed from the apparatus. THF was then distilled into the n-butyllithium and the TPM solution was added from the ampule through the breakseal. The solution started turning red almost immediately and was allowed to stir at room temperature for 8-10 hrs. THF was then distilled from the solution into the trap leaving behind the dark red TPML. The apparatus was then cooled to -78°C and dried hexane was distilled into the flask (THF:Hexane approximately 1:15). The apparatus was sealed from the line and the recrystallized TPML was washed with the hexane. This was accomplished by pouring the hexane from the main body of the apparatus into the wash ampule and distilling back into the main body. After repeating this procedure several times the hexane was removed from the main body in the wash ampule.

The apparatus was reattached to the line and THF was distilled in to dissolve the TPML salt. The TPML solution was poured into a separate

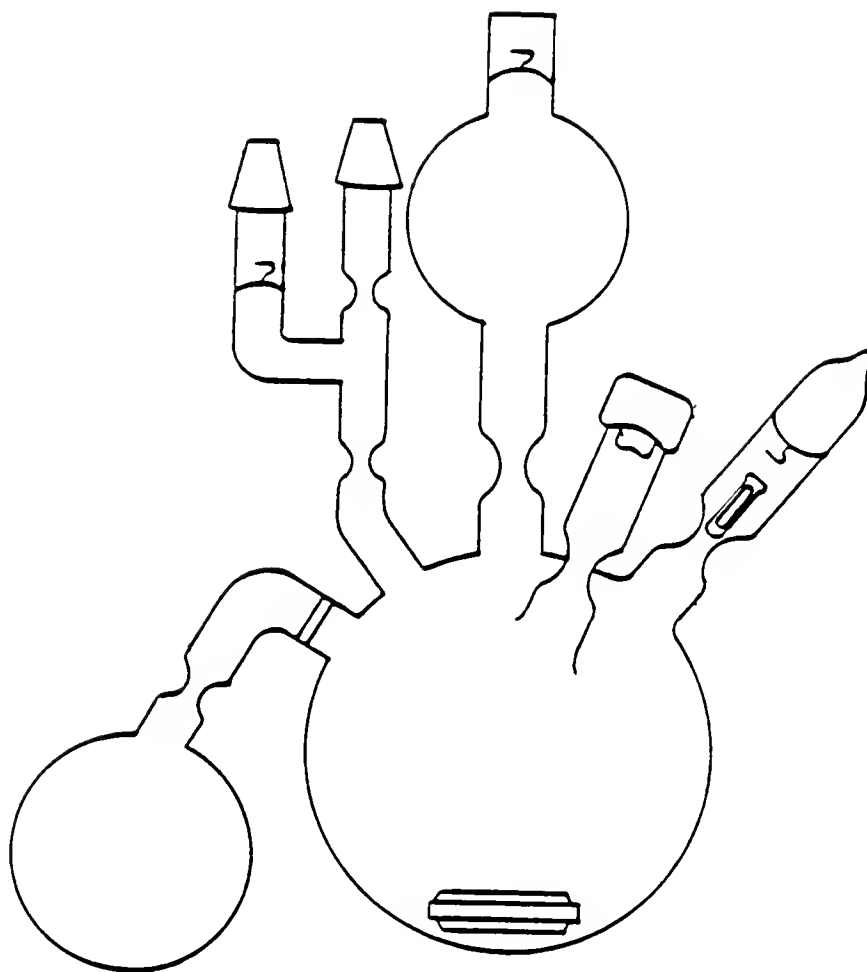


Figure 2-3. Apparatus used for the preparation of TPML.

ampule and sealed off from the main body. The initiator was stored at -20°C and was further divided as needed. The concentration of the initiator was determined as described later.

1.1 Diphenylhexyllithium (DPHL)

DPHL [33] was prepared by reaction of equimolar amounts of 1,1-diphenylethylene and n-butyllithium in THF at room temperature for 12 hrs. The reddish orange salt was purified by washing with hexane as described for TPML. The THF solution of DPHL was stored at -20°C and divided as needed. The concentration of the initiator was determined as described later.

Triphenylmethylpotassium (TPMK)

TPMK was synthesized by reaction of a 1.1-molar excess of a solution of TPM in THF with a solution of oligomeric dianions of α -methylstyrylpotassium (α MSK) in THF prepared by reaction of α -methylstyrene in THF with potassium metal for 24 hrs at 25°C [34].

A THF solution of TPM was prepared in vacuo in a breakseal equipped ampule. The red solution was filtered through a frit and divided into ampules. The THF solutions of TPM and α MSK were reacted with each other in vacuo at room temperature for 2 hrs. After the reaction the TPMK solution was sealed from the line and divided into various ampules. The concentration of the TPMK solution was measured as described later.

1-Lithio-1-(Phenylsulfinyl) Ethane (EPSL)

EPSL [1, 2] was synthesized by a reaction of a 1.1 excess of ethylphenylsulfoxide with methyllithium in THF at -78°C . The apparatus used for the synthesis is illustrated in Figure 2-4. The apparatus was attached to the line and evacuated. Argon was then charged into it through the line and methyllithium was injected through the serum cap. The

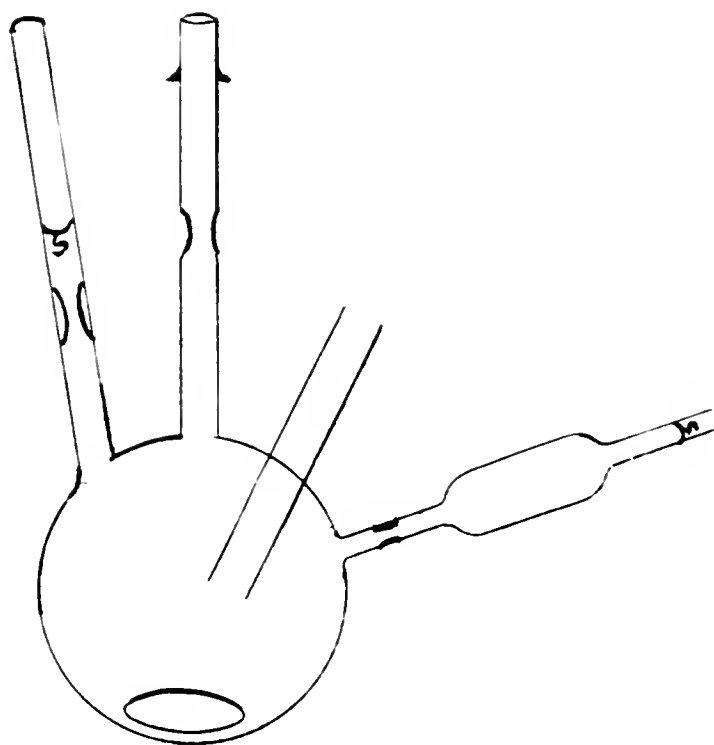


Figure 2-4. Apparatus used for the synthesis of EPSL.

solvent was carefully removed by distillation into the trap as the solution tended to bump in the apparatus. The serum cap was sealed off and THF was distilled to make a solution of methyllithium. The solution was then cooled to -78°C and ethylphenylsulfoxide was added from the ampule through the breakseal. The solution started becoming yellowish as the methyllithium reacted with ethylphenylsulfoxide to form the carbanion. The solution was degassed several times to remove the methane gas and was stirred at -78°C until no more methane gas evolved (as evidenced by the bubbling of the solution upon degassing and the characteristic pump noise). The yellowish-green solution was sealed from the line and poured into a side ampule which was sealed off. The initiator was stored at -20°C and divided as needed. The concentration of the initiator was determined as described below.

Determination of Concentration of Carbanions

For polymerization reactions concentration determination of metal alkyls and the delocalized carbanion salts was necessary. Thus, for anionic polymerizations in the absence of terminating impurities the number average molecular weight can in principle be predicted if the accurate concentration of the initiator is known. Also for two-ended carbanions the accurate determination of the concentration was imperative in order to prove the "two-endedness" of the system. Two methods were used for determination of concentration of initiators. The agreement between the two methods was found to be excellent ($\pm 5\%$).

Titration with Fluorene

The fluorene (Aldrich) used in titrations of the carbanion solutions was purified by crystallization from ethyl alcohol and pumped on the

vacuum line for several days to get rid of the traces of alcohol. Purity was better than 99% by GC.

The carbanion solutions in THF are reacted with a known excess of fluorene in THF at -78°C . In most cases the reaction of the carbanions with fluorene was instantaneous as seen by an immediate color change of the solution to yellowish-orange, the characteristic color of fluorenyllithium. The fluorenyllithium was then reacted with an excess of methyl iodide to form 9-methylfluorene and the ratio of fluorene to 9-methylfluorene was determined by capillary GC.

Determination of Concentration by UV/Visible Spectroscopy

UV/Vis was found to be an excellent method for concentration determination since most delocalized carbanions have distinct and strong absorptions in the visible region.

All of the absorbance measurements were carried out under high vacuum using an apparatus equipped with a UV cell. The absorbance of the unknown carbanion was measured followed by a reaction with an excess of fluorene. The absorbance of the fluorenyl carbanion thus formed was measured. Comparison of the two absorbances and the molar absorptivity of the fluorenyl carbanion from the literature [35, 36, 37] provided the molar absorptivity and hence the concentration of the unknown carbanion solution. This technique was found to be most convenient for solutions of living polystyryllithium capped with 1,1-diphenylethylene. The capped solutions are quite stable at room temperature during the time of spectroscopic determination and it also avoids the problem associated with the entrapment of fluorene and 9-methylfluorene in the polymer matrix during precipitation of the polystyrene in methanol (Method I).

The ampule containing the carbanion solution was attached to an apparatus which was provided with a quartz cell having a 2 mm path length, in conjunction with a 1.9 mm spacer. The whole system was attached to the line, evacuated, flamed and sealed off the line. The carbanion solution was introduced in the cell from the ampule through the breakseal and scanned in the visible and near UV regions. The fluorene was then introduced. A change in color was noted as the carbanion reacted with the fluorene to form fluorenyllithium. After all the carbanion reacted the fluorenyllithium was scanned in the UV region.

Assuming Beer's law to be applicable to both the carbanion solutions [25] one can write the following equations:

$$A_x = \epsilon_x C_x l \dots\dots\dots 2-1$$

$$A_y = \epsilon_y C_y l \dots\dots\dots 2-2$$

$$C_y = A_y \epsilon_x C_x / A_x \epsilon_y \dots\dots\dots 2-3$$

where x refers to the unknown carbanion solution and y to the fluorenyllithium, A = absorbance, ϵ = molar absorptivity, C = concentration of the absorbing species, l = path length, determined using a known standard solution of Potassium Chromate ($\epsilon_{372\text{nm}} = 4815$) [37].

Since $C_x = C_y$ (assuming no inadvertent protonation of the carbanion during the reaction) we get $\epsilon_x = A_x / A_y \epsilon_y$. Knowing ϵ_x one can calculate the molar concentration of the unknown carbanion solution using the equation 2-3.

Polymerization of Phenylvinylsulfoxide

The homopolymerization of phenylvinylsulfoxide (PVS) was carried out using the apparatus illustrated in Figure 2-5. The system consists of two round bottom flasks "a" and "b" (100 ccs and 50 ccs respectively) joined together. The ampules containing the initiator (TPML, methyl lithium, DPHL etc) and the terminating agent (usually methanol) were

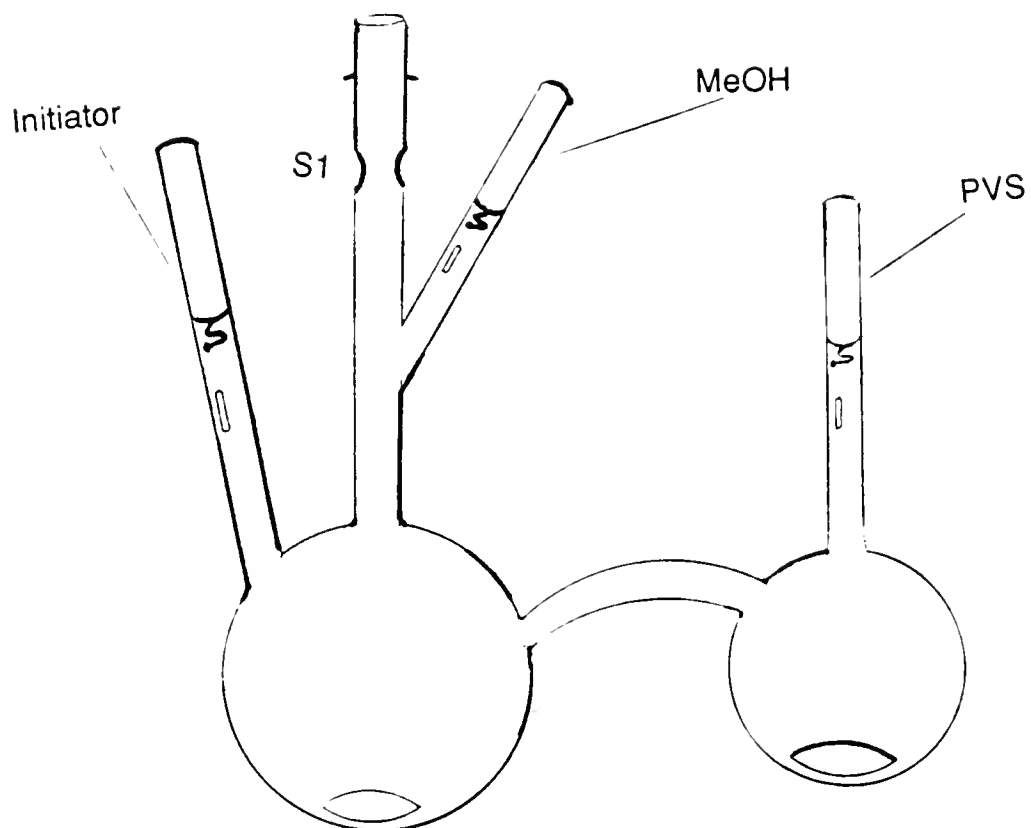


Figure 2-5 Apparatus used for the homo- and copolymerization of PVS.

attached to "a" along with a ground glass joint to hook it to the vacuum line. The monomer ampule is attached to the smaller flask ("b").

The apparatus was hooked to the vacuum line, evacuated and flamed thoroughly. The initiator solution was introduced into flask "a" through the break seal. The ampule was "washed" with the solvent using a cold cotton dauber in order to remove all of the initiator solution. Dried THF was then distilled in "a" to dilute the carbanion solution and the carbanion solution was thoroughly cooled to -78°C . The apparatus was then carefully sealed from the line at S1. The monomer breakseal was then broken and the monomer was introduced in the flask "b." THF was distilled into "b" from the carbanion solution. Care was taken to see that the initiator solution did not bump during the distillation. After sufficient dilution of the monomer both the initiator and the monomer solutions were cooled to -78°C as was the tube connecting the two flasks. The solutions were then rapidly mixed by pouring "b" into "a." An immediate change in color is usually seen, in the case of TPML from dark red to yellowish-green. This indicated that the initiation of PVS is quite rapid. After a few minutes more monomer is added. This procedure is repeated several times until all the monomer is consumed. The time of polymerization varied from 15 minutes to 12 hours. The yellowish-green color of the living α -phenylsulfinyl carbanion persists throughout the polymerization. The chain terminating electrophile (usually methanol) was then added to the polymerizing solution resulting in an immediate discharge of the yellowish-green color.

The solvent from the polymerization reaction was rotovaped down and the polymer was precipitated by pouring into a ten times excess diethylether solvent. The yield of poly(phenylvinylsulfoxide) (PPVS) was

determined by weighing and the polymer was characterized further by NMR, SEC etc. The PPVS was found to be thermally unstable and starts becoming yellow within a matter of days. It was thus found necessary to store the polymer in the freezer under argon.

\pm Poly(phenylvinylsulfoxide): ^1H NMR (CDCl_3 , 200 MHz, δ in PPM):

1.1-2.1 (2H), 2.5-3.5 (1H), 7.2-8 (5H)

\pm Poly(phenylvinylsulfoxide): ^{13}C NMR (CDCl_3 , 50 MHz, δ in PPM): 26-

32 (methylene in the chain), 56-60 (methine), 123-126, 128-130, 131, 140-142 (aromatic carbons)

(+) Poly(phenylvinylsulfoxide) $[\alpha]_D^{20} = 408$: ^1H NMR (CDCl_3 , 200 MHz, δ in PPM): 1.3-2.3 (2H), 2.7-3.6 (1H), 6.7-7.7 (5H)

(+) Poly(phenylvinylsulfoxide): ^{13}C NMR (CDCl_3 , 50 MHz, δ in PPM):

55-57 (methylene), 23-26 (methine), 123-126 (aromatic meta carbons), 128-130 (aromatic ortho carbon), 130-132 (aromatic para carbon), 140 (substituted aromatic quaternary carbon).

PPVS upon oxidation to poly(phenylvinylsulfone) (PPVO) becomes stable to air (or thermal) degradation. PPVS was oxidized to PPVO by hydrogen peroxide [1, 2, 38]. The polymer was dissolved in glacial acetic acid. An excess of 30% hydrogen peroxide was added. The polymer solution was allowed to stir at room temperature for 12 hrs. A bright white ppt was formed upon completion of the oxidation. The resulting PPVO was found to be insoluble in most solvents and partially soluble in chloroform and THF. Oxidation of the sulfoxide to the sulfone was seen to be quantitative by IR measurements and also by XPS (see Chapter 4).

Copolymerization of Styrene and Phenylvinylsulfoxide

A-B Copolymers

A-B copolymerization of styrene and PVS was carried out in two steps: (a) Polymerization of styrene was first carried out at -78°C in THF initiated by t-butyllithium [25] followed by capping with 1,1-diphenylethylene (1,1-DPE) followed by division of the capped living polystyryllithium into various ampules. (b) Polymerization of various amounts of phenyl vinyl sulfoxide was then carried out by using the capped living polystyryllithium as the initiator.

Polymerization of styrene was carried out in an apparatus illustrated in Figure 2-6. Once again the basic apparatus consists of 2 round bottom flasks "a" and "b" (500 ml and 50 ml respectively). The ampules containing the initiator (t-butyllithium) and the capping agent (1,1-DPE) are attached to flask "a." The monomer (styrene) ampule is attached to flask "b." The flask "b" is connected to "a" with a tube which extends into "a" at the top forming a lip. Additionally there are 2 ampules A1 and A2 equipped with breakseals having volumes 10 ml and 100 ml respectively.

Once the apparatus was assembled it was attached to the vacuum line through the ground glass joint, evacuated, checked for pinholes and flamed. The initiator was added from the ampule through the breakseal into flask "a" and washed down using a cold dauber. THF was then distilled into the initiator solution by cooling flask "a." The color of t-butyllithium turned yellow upon distillation of THF. This was probably due to deaggregation of the t-butyllithium in going from hexane to THF. It is also known that t-butyllithium reacts with THF at 25°C to form various alkoxides [25]. However the yellow color observed was probably not due to

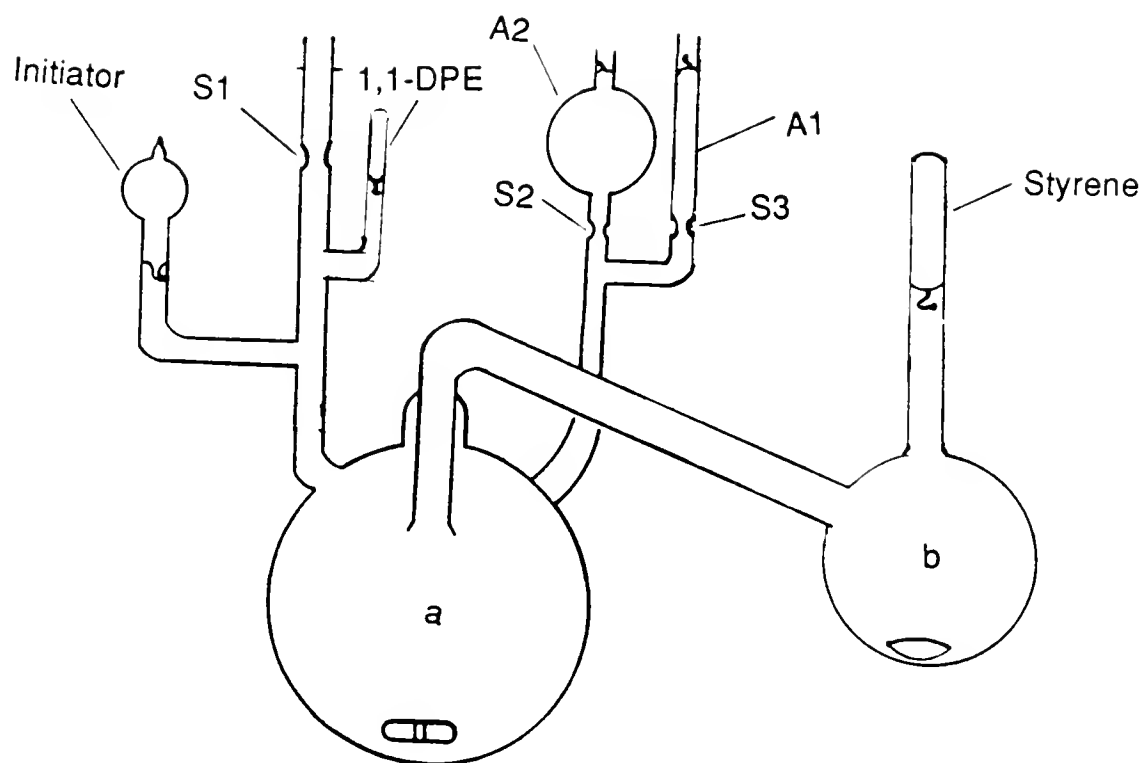


Figure 2-6. Apparatus used for the polymerization of styrene.

this reaction since the solution was kept at -78°C at all times. Several precautions were taken before styrene was distilled in; the level of the isopropanol/dry ice bath was kept below the level of the initiator and the path between the flasks "a" and "b" was kept warm using an air dryer. These precautions were warranted to make sure of a uniform vapor phase distillation of styrene into the rapidly stirring initiator solution and to avoid any local concentration of the monomer which is undesirable. The excellent molecular weight distributions bear testimony to the correctness of this technique (see Chapter 3). The breakseal of the styrene ampule was broken and styrene was slowly distilled from the flask "b" which was cooled to -20°C . The color of the t-butyllithium solution turned cherry red instantaneously. After all the styrene was distilled into "a" the solution was further stirred for 10 to 15 minutes. 1,1-DPE was then added to the living polystyryllithium solution. The cherry red solution turned dark red upon reaction. The apparatus was sealed off the line at S1. The solution was allowed to warm up and was then carefully poured into the side ampules. The constrictions S2 and S3 were washed using a cold dauber and the ampules were sealed off the main body.

Ampule A1 was used for the detection of the concentration of the living carbanions by UV/Visible spectroscopy and terminated by an electrophile like fluorene or methanol. The polystyrene was precipitated in an excess of methanol nonsolvent and characterized using SEC and NMR.

^1H NMR (CDCl_3 , 200 MHz, δ in PPM): 0.6 (d, t-butyl), 1.2-1.8 (2H), 1.6-2.3 (1H), 6.3-6.9 (2H), 6.8-7.3 (3H).

^{13}C NMR (CDCl_3 , 50 MHz, δ in PPM): 40-41 (methylene), 42-48 (methine), 125.8 (para aromatic), 127 (ortho aromatic), 128 (meta aromatic), 145 (substituted quaternary).

Ampule A2 was further attached to a divider (Figure 2-7), thoroughly evacuated, flame degassed and sealed from the line. The carbanion solution was introduced into the apparatus and was carefully divided into the various ampules. After washing the constriction of each ampule the divider was cooled in a large dewar to -78°C and each arm was carefully sealed off.

The polymerization of phenylvinylsulfoxide initiated by the living DPE capped polystyryllithium was carried out as described before for homopolymerization. The length of the styrene block was kept constant whereas the length of the poly(phenylvinylsulfoxide) was varied. The composition of the block copolymer was calculated from the moles of styrene and PVS used for each polymerization. The mole ratio of phenyl vinyl sulfoxide / styrene was varied between 0.26 to 8.0. The apparatus was the same as that for the homopolymerization of PVS (Figure 2-5). Once again a color change from dark red to yellowish-green was noticed upon addition of the monomer to the initiator and the living copolymer turned colorless upon termination with methanol. The copolymer was purified by precipitation in a solvent system comprised of ethyl ether and methanol (75/25 v/v).

^1H NMR (CDCl_3 , 200 MHz, δ in PPM): 0.6 (t-butyl), 1.2-1.8 (methylene of both polystyrene and poly(phenylvinylsulfoxide) blocks), 1.5-2.4 (methine of polystyrene block), 2.5-3.5 (methine of poly(phenylvinylsulfoxide) block), 6.3-6.9 (2H, ortho aromatic of polystyrene block), 6.7-7.5 (3H, meta and para aromatic of polystyrene block), 7-8 (5H, poly(phenylvinylsulfoxide) block)

The copolymer was stored in the freezer and characterized by SEC and by NMR. Conditions for oxidation of the copolymer were the same as

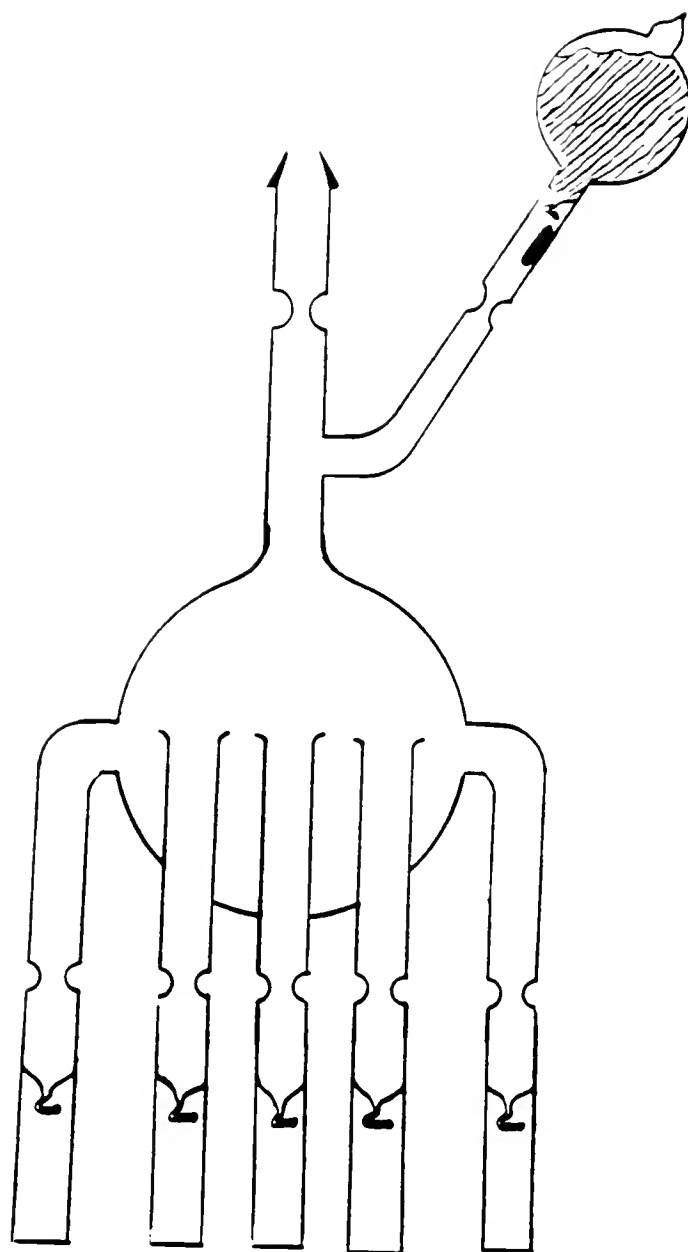


Figure 2-7. Apparatus employed for division of a carbanion solution into several smaller ampoules.

that for the homopolymer using an excess of 30% hydrogen peroxide for 24 hrs, yielding the thermally stable poly(styrene-b-phenylvinylsulfone).

A-B-A Triblock Copolymers

The A-B-A copolymers of styrene and phenylvinylsulfoxide like the AB copolymers were prepared in two steps: (a) formation of living two-ended polystyryllithium using lithium naphthalide initiator [39] followed by capping with 1,1-DPE and division of the capped living polystyryllithium into various ampules and (b) polymerization of various amounts of PVS using DPE capped two-ended polystyryllithium.

Living two-ended polystyryllithium was prepared in a manner similar to the polymerization of styrene using t-butyllithium described before. Lithium naphthalide was employed as the initiator. After assembling the apparatus (Figure 2-6) it was attached to the vacuum line, evacuated, checked for pinholes and flame degassed. The initiator solution was introduced into "b" and cooled to -20°C . The usual precautions were taken during distillation of styrene in the polymerization solution as described before. An immediate color change from dark green to cherry red was seen upon addition of styrene. After all of the styrene was distilled the solution was further stirred at -78°C for 15 minutes. 1,1-DPE was then added to the living polystyryllithium. The cherry red color changed to dark red upon reaction with 1,1-DPE. The apparatus was sealed from the line and the solution was divided into two ampules as described earlier. The determination of concentration and workup were similar to that of the one-ended system.

The second step in the triblock copolymerization was identical to the diblock. Once again the styrene block length was kept constant whereas the phenylvinylsulfoxide block length was varied depending on the moles of

styrene used and the ratio of phenylvinylsulfoxide to styrene desired. Workup of the triblock copolymer was same as that of the diblock.

Monomer Conversion Study

It was found necessary to roughly determine the conversion of monomer with time, so as to have a rough idea of the kinetics of the polymerization reaction. Since aliquots of the polymerization mixture were withdrawn at various times during the polymerization, the polymerization had to be carried out under rigorously dried argon.

Naphthalene was employed as an internal standard in order to monitor the consumption of monomer with time. Several factors were considered for using naphthalene as an internal standard. Naphthalene and PVS have retention times in GC which are quite different and measurable. A calibration curve of ratio of moles of phenylvinylsulfoxide to naphthalene versus the GC ratio of the areas of PVS to naphthalene (Table 2-1) gave a straight line with an excellent correlation coefficient (Figure 2-8). Also naphthalene is inert in presence of living the PPVS carbanions.

The apparatus used during the above polymerization was similar to Figure 2-5 and consisted of 2 bulbs "a" and "b" joined together. The initiator ampule was attached to "a" along with a high vacuum stop-cock. To the flask "b" was attached a monomer ampule and a short outlet with a rubber septum for aliquot withdrawals. The apparatus was attached to the vacuum line and the absence of pinholes was checked. Purified argon was charged to the apparatus and a known amount of naphthalene was added to flask "b" which was then evacuated again. Care was taken to see that none of the naphthalene sublimed to the trap under the high vacuum. The initiator was introduced in flask "a" and the contents of the ampule were washed down. Additional THF was distilled into the initiator solution

Table 2-1. Calibration for the determination of phenylvinylsulfoxide in the presence of naphthalene as an internal standard.

mol PVS x 10 ⁴	mol NPH x 10 ⁴	mol PVS/mol NPH	A PVS/A NPH
6.1	1.7	3.6	2.56
5.7	4.3	1.3	0.96
7.7	7.7	1.0	0.68
5.9	9.7	0.61	0.39
5.7	12.2	0.47	0.33
6.5	15.3	0.42	0.31

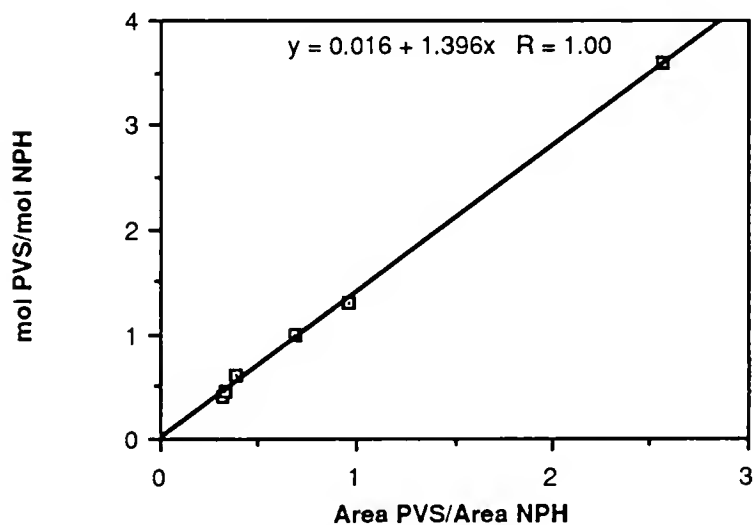


Figure 2-8. Graph of ratio of moles of PVS to Naphthalene versus ratio of areas (in GC) of PVS to Naphthalene.

through the vacuum line. The monomer was then introduced into "b", and diluted with THF by distillation from the initiator. Both "a" and "b" were cooled to -78°C . Argon was charged into the apparatus, through the line. The argon had to be rigorously dried, which was accomplished by using a solid KOH and drierite traps followed by a cold (-78°C) trap. The stopcock S between the line and the apparatus was closed off and the apparatus detached from the line. Both the flasks were then cooled to -78°C . The initiator solution was introduced into flask "b" by tilting the apparatus. Aliquots of the polymerization solution were withdrawn at various times during the polymerization through the rubber septum using a syringe and were quenched in methanol. The quenched solution was added to an excess of diethyl ether to precipitate the polymer, which was filtered and the filtrate was rotovaped and analyzed by GC so that the change in concentration of monomer with time could be determined. The polymer was dissolved in THF and analyzed by SEC for the change in polymer molecular weight with time.

Thermal Elimination

Thermal elimination of the homo- and copolymers in the solid state was carried out using a Thermolyne tube furnace with a suitably equipped pyrolysis tube (Figure 2-9). The polymer was dissolved in a minimum amount of THF or chloroform. The solution of the polymer was introduced into the section "a" using a pipette. The tube was attached to a rotovap in a horizontal position and was evaporated with a gradual application of vacuum. The application of vacuum and slow rotation ensured a thin uniform film surface in the section "a." The tube was then inserted into the Thermolyne furnace and hooked to the vacuum line. A cold (-78°C) trap was used between the line and the tube to trap any condensables.

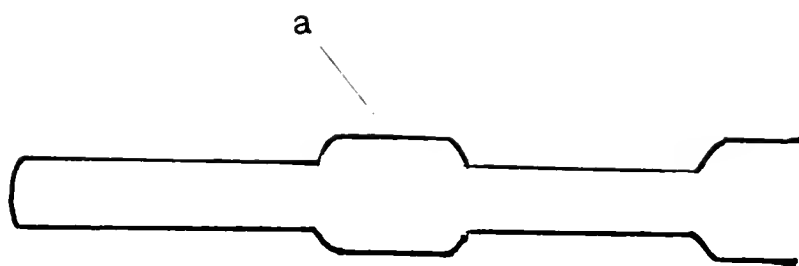


Figure 2-9. Pyrolysis tube used for the thermal eliminations of the homo- and copolymers in the Thermolyne tube furnace.

Elimination was carried out by gradually increasing the temperature to 180-200°C and under high vacuum (10^{-6} torr) for 1.5 hrs. The polymer after heating became dark black and shiny and was handled under argon (glove bag) at all times. The eliminated products obtained from the side of the tube outside the furnace were analyzed by MS, GC, and NMR.

Instrumental Methods

Size Exclusion Chromatography (SEC)

SEC was carried out on a Waters 6000-A liquid chromatograph Phenomenex (Rancho Palos Verdes, CA) TSK Gel G-3000H and G-5000H columns were employed in series (column dimensions: 75mm x 30cm). The columns were packed with spherical, crosslinked poly(styrene divinyl benzene) particles having pore sizes 10^3 Å and 10^5 Å for G3000H and G5000H respectively. The molecular weight limits for G3000H were 600 to 60,000 and that for G5000H were 10,000 to 10^6 . Polystyrene standards were supplied by Scientific Polymer Products, Polysciences INC., Pressure Chemical Co. and Waters Associates. The standards ranged from a molecular weight of 2000 to 2,00,000. All polymer solutions injected in the columns were filtered through a 0.5 µ PTFE filter ("Alltech", IL.).

The eluting solvent was HPLC grade THF filtered through a 0.5 µ filter. The flow rate was usually 1 ml/minute. The model 6000A solvent delivery system by "Waters Associate" was utilized. Injection into the column was achieved by a Waters Associate Model U6K universal liquid chromatograph injector which allowed loading and injecting samples at a pressure of up to 600 psi without interruption of the solvent flow. A Perkin-Elmer LC-75 spectrophotometric UV detector set at 254 nm was used for detection of the eluting polymer. The detector was interfaced with a Zenith PC-100 personal computer equipped with a MS-DOS Dascon-1

data collecting program operating at a rate of 1 Hz. The Basic programs used for data acquisition, molecular weight calibration, computation of molecular weight averages and distributions were written by W. Toreki in our group [40]. The Basic program for the conversion of the data into a high resolution graphics display was written by the author with help from Dr. Gardiner Myers. Explanations of these Basic programs and the relevant analytical chemistry involved with it are described elsewhere [40].

A calibration curve was created by injecting various polystyrene standards and using a correction factor to account for band broadening. The retention volume of PPVS was then compared to the calibration curve and an apparent molecular weight for our system was determined. In the absence of suitable PPVS standards this method was found to be quite accurate for determination of apparent molecular weight and molecular weight distribution of PPVS homopolymers and its copolymers with styrene.

Capillary Gas Chromatography (GC)

Routine analyses of monomers and reagents were done by GC. A Hewlett-Packard 5880A gas chromatograph was used for this purpose. The system consisted of a 50 meter (G. E. Co. SE-54) fused silica capillary column (0.2mm ID) coated with a 0.11 μ M film of silicone gum, a microprocessor capable of automation, a temperature programmable oven and a flame ionization detector. Helium was used as the carrier gas. A stepwise gradient temperature program was used so that the oven temperature increased at a controlled rate for higher resolution.

Nuclear Magnetic Resonance Spectroscopy (NMR)

Proton and Carbon-13 NMR spectroscopy was used as an extensive tool for structure determination, determination of purity of reagents, for

characterizing the microstructure in the copolymers and also for monitoring the change in the structures of the homo- and copolymers upon heating. Most of the NMR spectra were recorded on a Varian FT-NMR XL 200 spectrometer featuring distributed microcomputer control and a flexible, high-storage-capacity memory capable of high resolution Fourier transform. Deuterated chloroform was used as a solvent in most monomer and polymer studies. The chemical shifts were reported in PPM using TMS as a reference.

High temperature NMR was done on a Varian XL-300 NMR spectrometer featuring the same software as the XL-200. Acetic acid-D4 was used as a solvent. A heavy-walled 5 mm tube was employed and the polymer solution was sealed under a partial pressure under argon. The spectra were recorded at room temperature and the temperature was increased in steps of 20°C. A nitrogen atmosphere was used in the probe. Spectra were recorded at 60, 80, 100, 120, 140, and 150°C.

Infrared Spectroscopy (IR)

Infrared spectroscopy was used for additional structure determination of the polymers, determination of oxidation of sulfoxide to sulfone and monitoring of the thermal degradation of PPVS. Routine measurements were carried out using a Perkin-Elmer 281 IR spectrophotometer using a pressed KCl pellet or a NaCl window coated with the polymer. Spectra were also recorded on a Nicolet 5DXB FT-IR spectrophotometer using NaCl windows under a nitrogen atmosphere. High temperature IR runs were carried out by Ms. Jennifer Lin in the materials science department. Spectra were recorded on a Nicolet 60SX FT-IR spectrophotometer equipped with an "Omega" temperature controller. The polymer was mixed in diamond powder, mounted and heated under nitrogen

atmosphere. The temperature was increased to 200°C over a period of time at a heating rate of 5°C/min and the spectra were recorded continuously.

UV/Visible Spectroscopy

UV/VIS spectroscopy was used for determination of concentration of carbanions. A Perkin-Elmer Lambda-9 UV/VIS/NIR spectrophotometer was employed. Quartz cells having a 2 mm path length were used in conjunction with a quartz spacer. The path length was calibrated using a known standard solution of potassium chromate. The cells were usually attached to the reaction vessel and the spectra recorded under high vacuum. A special spectrometer cover was made by the chemistry department machine shop designed to prevent extraneous light to interfere with the measurement. The spectra were usually scanned from 700 nm to 300nm. THF was the solvent in most cases. The response time was 1 second, scan speed 120 nm/min, peak threshold 0.02 Å, cycles/time 1/0.05 min, using an automatic lamp.

Polarimetry

The optical activity of the optically active monomer and polymer was measured using a Rudolph Research Autopol III automatic polarimeter.

Pyrolysis-Mass Spectrometry

Pyrolysis-MS was used as a technique for characterizing the thermal elimination on the homo- and copolymers. It was carried out by Dr. King in the mass spectrometry laboratory. The mass spectrometer used for this purpose was the AEI MS-30.

The polymer was inserted using a direct insertion probe. A gradient temperature from 100 to 500°C was employed. Spectra were recorded continuously at various temperatures and processed by a "Kratos" data system.

Thermogravimetric Analysis (TGA)

TGA was carried out on a Perkin-Elmer TGA7 thermogravimetric system. The system consists of the TGA7 thermogravimetric analyzer controlled by the TAC7 thermal analysis instrument controller. The analyzer permits the measurement of weight changes in a sample material resulting from chemical reactions, decomposition, eliminations etc as a function of either temperature or time.

The heart of the thermal analysis system is the 32 bit PE-7500 professional microcomputer which allows for totally computerized control of the TGA7 analyzer. Thus the TGA7 can be programmed to scan a temperature range by changing at a linear rate over several temperature ramps or it can analyze data at isothermal temperatures to measure weight loss/gain with time.

The TGA7 analyzer is made up of 2 major components: a sensitive ultramicrobalance and a furnace element. Other components of the system include the GSA-7 gas selector accessory and the graphics plotter.

Before each session the analyzer balance and the furnace were calibrated over the temperature range used. A curie point temperature calibration was also carried out using 2 standards: Alumel (163°C) and Perkalloy (596°C). The polymers were usually scanned under a nitrogen sample purge (50 ml/min) from 50°C to 900°C at a heating rate 10°C/min.

X-Ray Photoelectron Spectroscopy (XPS)

XPS (also known as Electron Spectroscopy for Chemical Analysis or ESCA) was used for the determination of the surface composition of the homo- and copolymers, the determination of oxidation of sulfoxide to sulfone, and the observation of changes on the surface of the polymers upon thermal treatment. A Kratos XSM-800 x-ray photoelectron

spectrophotometer was employed for the measurements. All the measurements were done by Mr. Richard Crockett in the material science department. The instrument consisted of 2 chambers: (i) sample treatment chamber and (ii) sample analysis chamber.

The sample was mounted as a film on a 10-sample carousel. Automation allowed analysis of 10 consecutive samples during a run. Once the sample is mounted the sample treatment chamber is evacuated. A rotary oil pump in conjunction with a turbomechanical pump and a cold trap makes it possible to attain vacuum in the order of 10^{-8} Torr routinely. The sample is transferred into the sample analysis chamber only after a vacuum of 10^{-8} Torr is attained in both of the chambers.

The sample is irradiated with a low energy Mg K-alpha (1253.6 eV) X-ray photoelectrons. The kinetic energy of the electron emitted due to the interaction of the X-rays with the atomic orbital electron is measured and the binding energy of the electron is calculated. The binding energies of the various elements are standardized using the C_{1s} peak (285 eV) as the reference. The instrument is occasionally calibrated using a thin silver foil (Ag_{3s} 368 eV).

High temperature XPS was carried out using a fast insertion stainless steel probe mounted on a copper block. The polymer was mounted on the copper block, introduced in the sample treatment chamber and evacuated. The sample was scanned at room temperature and heated in the sample treatment chamber to 100°C for 0.5 hrs. The thermocouple was standardized to the sample temperature (50°C differential). After all the condensables were removed as registered by the vacuum in the chamber (10^{-7} to 10^{-8} Torr) the sample was introduced in the analysis chamber and scanned. A similar procedure was followed at 200°C and 300°C.

Contact Angle of PPVS Homo- and Copolymers

Contact angle is a measure of the surface free energy of PPVS homo- and copolymers. Measurement of the contact angle was carried out by the captive air bubble method. The polymer was dissolved in chloroform, coated on a glass slide and was thoroughly pumped in the vacuum oven to get rid of residual solvent. The coated slide was immersed in water and constant volume air bubbles were delivered between the polymer film and the water surface using a 5 μ l syringe. The contact angle of the air bubble between the polymer film and the water surface was measured after 30 s. A number of observations were made and the mean of the values was taken. The contact angle is inversely proportional to the surface free energy. Thus the higher the contact angle the lower is the surface free energy.

CHAPTER 3 HOMOPOLYMERIZATION AND COPOLYMERIZATION OF PVS

Homopolymerization

The polymerization of phenylvinylsulfoxide (PVS) was investigated. Most of the polymerization studies were carried out on the racemic monomer. However the optically active monomer was also investigated albeit not as thoroughly.

Attempts were made by Mulvaney and Ottaviani to polymerize R-(+)-isopropenyl p-tolyl sulfoxide using various anionic and radical initiators which were unsuccessful [41]. Homopolymerization of R-(+)-p-tolylvinylsulfoxide was also attempted using initiators such as benzoyl peroxide, azobisisobutyronitrile, n-butyllithium and boron trifluoride etherate. Once again their attempts failed. n-Butyllithium most likely attacked the sulfur displacing the aryl group [42] and thus failed to polymerize the monomer. Kunieda et al. [43,44] tried polymerization of optically active p-tolylvinylsulfoxide using n-butyilmagnesium bromide as initiator. This gave an optically active polymer of a molecular weight of 2400. However they obtained very poor yields (10%). The successful polymerization of PVS has recently been carried out using methyllithium as initiator in THF at -78°C [2].

In the present work the polymerization of PVS was carried out by mixing a solution of the initiator and monomer in THF in vacuo at -78°C. Various initiators were tried initially for the polymerization and are summarized in Table 3-1.

Table 3-1. Homopolymerization of PVS Using Various Anionic Initiators in THF at -78°C .

Initiator	Apparent Molecular Weights (Exptl) ^a		M_n Calcd ^b	M_w / M_n	Yield (%)
	M_w	M_n			
TPML	2679	2066	1979	1.33	95
	2747	2469	3200	1.11	60
	5945	4219	5328	1.41	92
	33100	24600	---	1.34	90
TPML ^c	4502	3310	3970	1.36	90
TPMK	8060	6063	12500	1.33	95
DPHL	1240	1171	6089	1.1	>70
Methyl-lithium	3025	2605	6241	1.16	94
	10309	7423	7537	1.39	95
	11261	7698	6729	1.46	90
	17811	12349	12177	1.44	84
EP SL	18384	15515	19976	1.18	75
	9751	7497	11873	1.3	70
	14418	11982	11720	1.2	86
LiNph	18982	14594	15222 ^d	1.3	90

a. From GPC using polystyrene standards

b. M_n Calcd. = [monomer] converted/[initiator] \times M_{monomer}

c. solvent system 1:1::THF:toluene

d. M_n Calcd. = [monomer]/[initiator] \times 2 \times M_{monomer}

Initiators

It is seen from the Table 3-1 that the delocalized carbanions viz triphenylmethyllithium (TPML), triphenylmethylpotassium (TPMK) and diphenylhexyllithium (DPHL) are excellent initiators. TPML was, in fact, the initiator of choice and most of the studies of the polymerization of PVS (kinetics, temperature effects, etc.) were carried out using this initiator. There were several reasons for the choice. TPML is very easy to synthesize (Chapter 2) from a quantitative reaction of triphenylmethane (which itself is a solid and easy to purify and handle) with *n*-butyllithium. The carbanion salt is extremely stable even at R.T. in vacuo (although we always stored it in the freezer). The solutions of TPML have an intense absorption in the visible region (ϵ at 500 nm = 31,000) so that their concentrations can be accurately measured by UV/VIS spectrometry. The intense color also helps in monitoring visually the initiation process since a dramatic change in color is seen in going from the TPML carbanion to the α -lithiosulfinyl carbanion (dark red to yellowish green). Also TPML is not nucleophilic enough to attack the sulfur atom in the monomer causing side reactions (at least at -78°C).

Methylithium was the only alkylithium successfully employed as the initiator [1, 2]. *n*-Butyl and *t*-butyllithium, interestingly, attack the sulfur atom causing an $\text{S}_{\text{N}}2$ displacement of the aryl group [42, 45-48]. This has also been documented [44, 47] in alkyl aryl sulfoxides where the alkylithiums other than methylithium prefer nucleophilic attack on the sulfur of the sulfinyl rather than proton abstraction.

Electron transfer initiators like lithium naphthalide were also employed for initiation. A two-ended polymerization of PVS was thus

achieved similar to conventional monomers like styrene [25]. Thus the initiation of polymerization of PVS appears to be similar to the conventional anionic polymerization for instance of styrene.

The dipole stabilized initiator 1-lithio-1-(phenylsulfinyl) ethane (EPSL) which is a carbanion analogous to that of the growing chain was also found to be an effective initiator giving polymers of controlled molecular weight and narrow molecular weight distribution. As will be discussed later polymeric initiators, both one-ended and two-ended can also be used as initiators to give block copolymers.

The initiation of PVS is instantaneous as seen from an immediate change in color from dark red (for the delocalized carbanion) to yellowish-green color of the growing α -lithiosulfoxide carbanion (Figure 3-1).

Nature of the Propagating Carbanion

The living α -sulfinyl carbanion has been shown to be a dipole stabilized ion pair in THF [2]. For instance the U.V. spectrum of ethylphenylsulfoxide (EPS) and the carbanion derived from it show almost no difference in the absorption maxima [2]. Also the ^{13}C NMR signals for the carbanion are almost the same as those of the parent hydrocarbon. Since delocalization of the negative charge into the aromatic ring would generally result in an upfield shift of the para carbon due to shielding [49-51], there appears to be little or no delocalization of the negative charge into the aromatic ring. Also the IR spectra of the carbanion of EPS and the parent hydrocarbon exhibit the same absorption wavelength for the S=O stretch [2]. All of these observations indicate the absence of delocalization of the negative charge into the S=O bond.

The bond moment of the S-O bond has been determined to be 4.76 D [51]. From the x-ray structure the S-O bond length in EPS was found to be

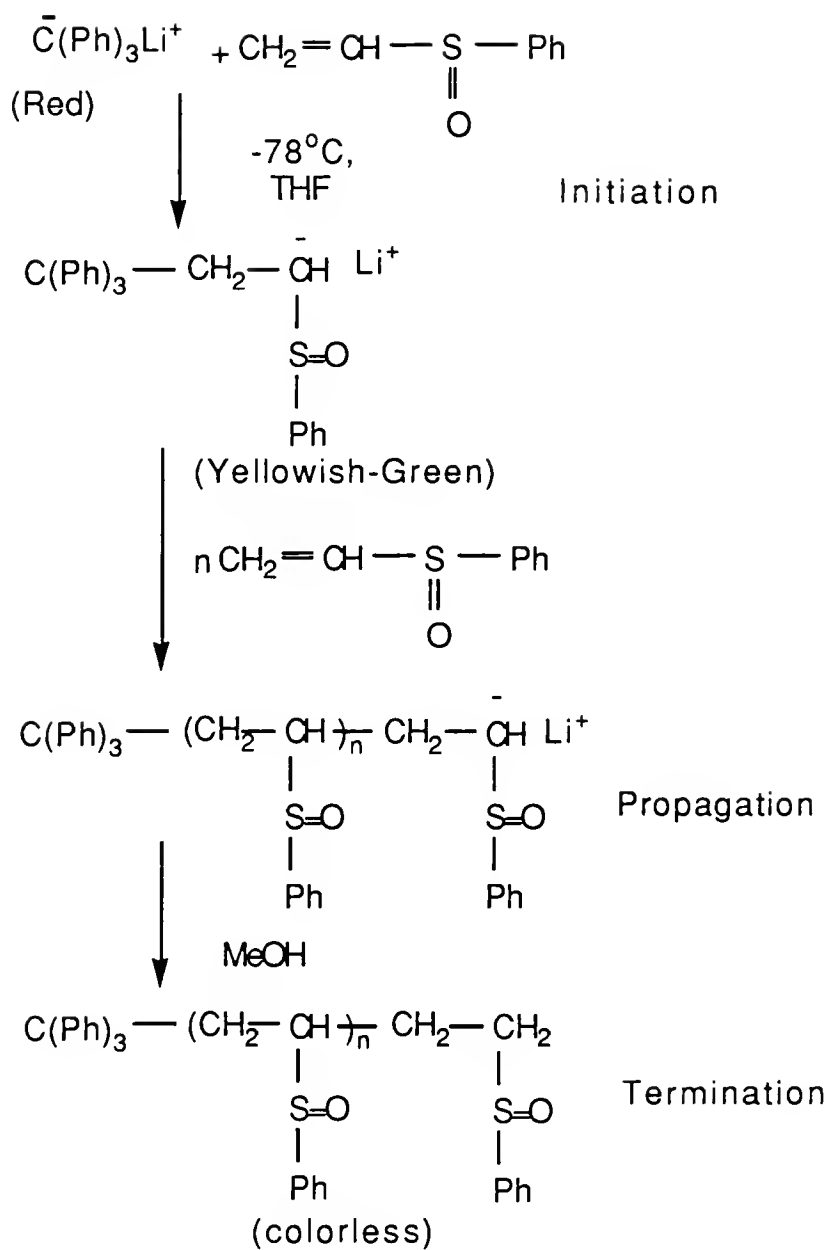


Figure 3-1. Homopolymerization of PVS.

1.47 Å [2]. Using the equation: $\mu = e d$, where μ is the dipole moment in debye, e is the magnitude of charge in ESU and d is the bond length. The magnitude of the apparent charges on oxygen and sulfur was thus found to be 0.67 electrons. Thus the S-O bond can be best described as a bond with substantial ionic character.

Elegant ^{13}C NMR studies by Marquet et al. [49-51] reveal that the $\Delta^1J_{\text{C-H}}$ in the α -lithio sulfoxide shows a large increase (+16.5 Hz) in ^{13}C NMR upon metalation of the α -carbon of methyl phenyl sulfoxide. Thus the carbon bearing the negative charge was shown to have a high sp^2 character similar to that found in Ph_2CHLi . In methyl phenyl sulfoxide it was found that the ^{13}C - ^1H coupling constant decreases in the cryptated potassium salt as compared to the uncryptated complex. Thus the carbanion becomes more pyramidal (or the sp^3 character increases) upon cryptation. This suggests that the planar sp^2 configuration is stabilized by interaction with the cation. It is therefore reasonable to assume a chelated structure (Figure 3-2) possible because of the high charge density present on the oxygen in the S-O bond. This internal chelate interaction is strong even for very polar solvents and is disrupted only upon using a very powerful chelating agent such as a cryptand [51].

The chelated structure is possible even for potassium which is expected to have a looser interaction with the anion. The α -potassio sulfoxide would be expected to have similar properties as the α -lithio sulfoxide. This is in fact what we find by using TPMK as initiator (Table 3-1). The molecular weight distribution which is a good indication of the efficiency of the initiation is similar to that for TPML. The effect of decreasing the solvent polarity from 100% THF to 1:1 THF: toluene would be expected to increase the anion-cation interaction. However we see little

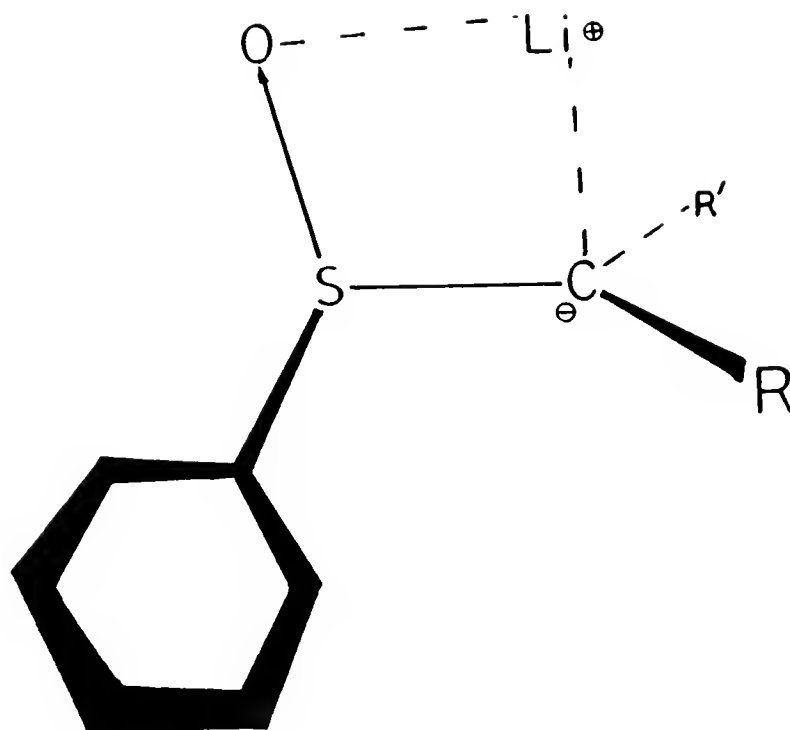


Figure 3-2. Chelated ion pair structure of α -sulfinyl carbanions with lithium as counter ion.

change in the SEC of the polymerization product in going to a less polar medium (Table 3-1).

Effect of Temperature

The effect of temperature in both the initiation and in the propagation reaction was found to be dramatic. A series of experiments were performed to explore the effect of temperature on the initiation and polymerization. The results of these experiments are summarized in Table 3-2.

In runs 1 and 2 two parallel polymerizations were carried out having similar concentrations of initiator and monomer. One of the polymerizations was initiated at -85°C and was allowed to propagate at -85°C using a mixture of dry ice and ethylether. The other was initiated at -25°C and kept at -25°C using a mixture of dry ice and carbon tetrachloride. Runs 3 and 4 were carried out by initiation and propagation at -78°C and 25°C (room temperature) respectively.

Run 5 was carried out in an apparatus which was provided with a side bulb connected through a high vacuum teflon stopcock. The reaction was initiated at 25°C and the solution was then immediately divided into two portions by pouring half of the reaction mixture in the side bulb through the high vacuum teflon stopcock. The stopcock was then closed off and the solution in the side bulb was quickly cooled to -78°C . The solution in the main body, however, was kept at 25°C . In this way one can see the effect of initiation at 25°C and propagation at -78°C and 25°C respectively.

Run #6 was similarly initiated at -78°C and divided into two portions; one was allowed to proceed at -78°C while the other was warmed up to 25°C . Run #7 was simply a repeat of run #6.

Table 3-2. Effect of Temperature on Polymerization of PVS. Initiated by TPML in THF.

Run #	T _i ^a °C	T _p ^b °C	M _w	M _n	M _n Calcd ^c	M _w /M _n	Distribution
1	-85	-85	10810	7595	19025	1.42	unimodal
2	-25	-25	11012	7127	19025	1.55	unimodal
3	-78	-78	5945	4219	5328	1.41	unimodal
4	25	25	8495	3751	4892	2.26	bimodal
5	25	-78	9178	3671	4033	2.5	bimodal
	25	25	8805	3108	4033	2.83	bimodal
6	-78	-78	6947	4533	4652	1.53	unimodal
	-78	25	6829	3949	4652	1.73	unimodal
7	-78	-78	4795	3138	4567	1.53	unimodal
	-78	25	4907	2392	4567	2.05	unimodal

a. Temperature of initiation.

b. Temperature of polymerization.

c. $M_n \text{ Calcd.} = [\text{monomer}]/[\text{initiator}] \times M_{\text{monomer}}$

Effect of Temperature of Initiation of PVS

It was seen that during initiation of PVS at 25°C the color changed from dark red (TPML) to yellowish-green, characteristic of the α -sulfinyl carbanion, and then once again to red within minutes. The color progressively became darker with time and did not discharge when the carbanion solution was reacted with methanol. An attempt made to monitor the formation of the colored side products using UV/VIS spectroscopy failed. Only a tail was seen in the visible region which gave no useful information as to the identity of the colored products.

The effect of temperature during initiation by TPML was of interest. It was seen that initiation at low temperatures (<-25°C) led to a unimodal distribution in the SEC chromatogram. However, initiation at 25°C gave rise to a bimodal distribution (Figure 3-3) even when the solution is cooled down to -78°C immediately after initiation (Figure 3-4).

This leads us to believe that at low temperatures the initiation process forms only one propagating species. However, at higher temperatures two distinct propagating or initiating species may be present: a major giving rise to the high molecular weight peak in SEC with a minor giving rise to the low molecular weight peak (Figures 3-3 and 3-4). Obviously the high molecular weight (major) initiating species propagates or initiates faster than the low molecular weight (minor) one.

It is seen from Table 3-1 that there is excellent agreement between the calculated and experimental M_n in most runs. This indicates that the "living" nature of the polymerization is similar to that of a conventional anionic polymerization for instance of styrene.

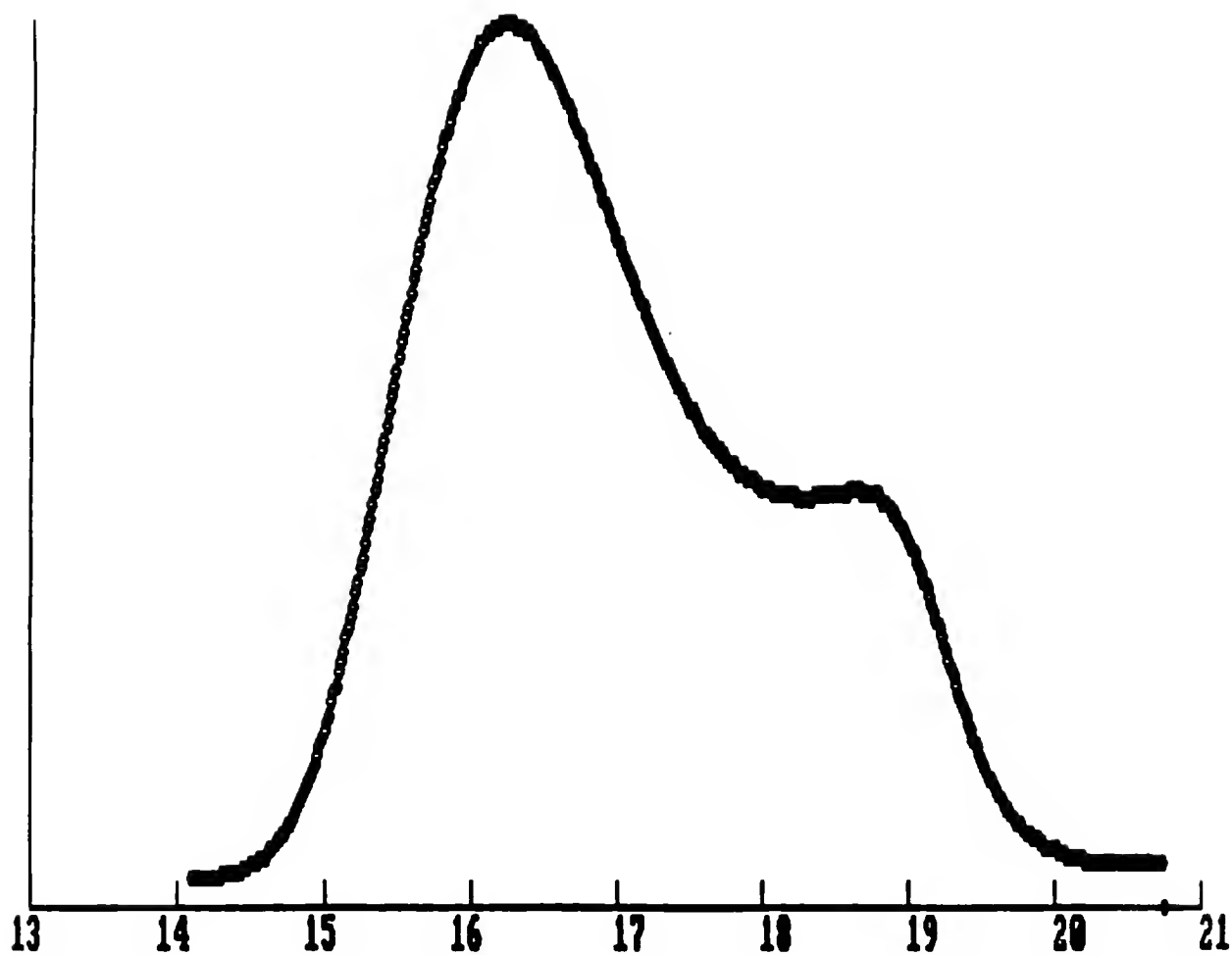


Figure 3-3. SEC chromatogram of PPVS initiated by TPML at 25°C and polymerized at 25°C in THF. Eluting solvent: THF. Flow rate: 1 ml/min.

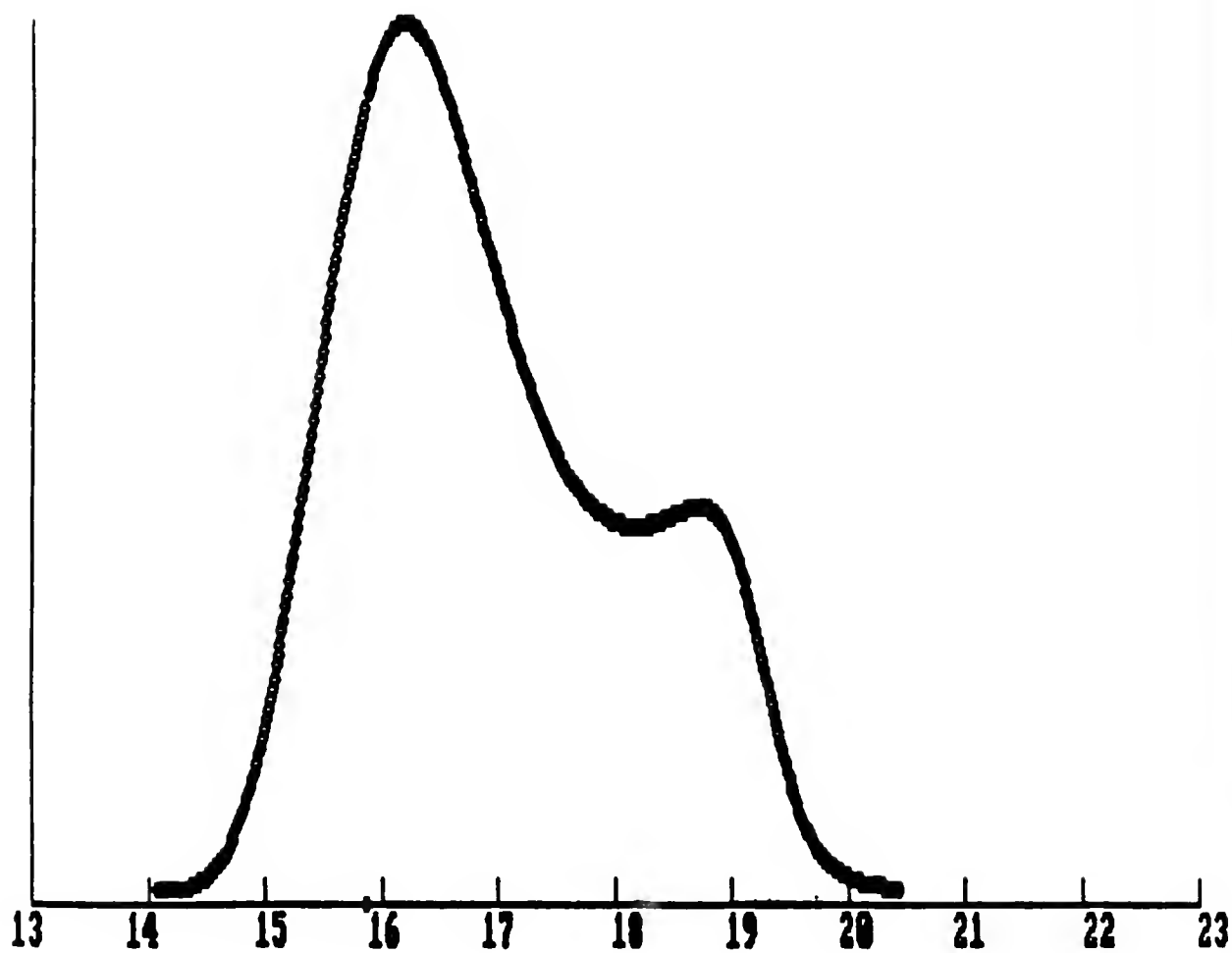
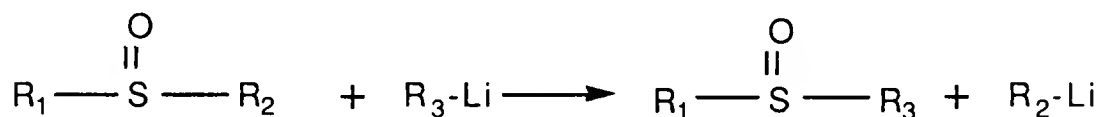


Figure 3-4. SEC chromatogram of PPVS initiated by TPML at 25°C and polymerized at -78°C in THF. Eluting solvent: THF. Flow rate: 1 ml/min.

Reactions of alkyllithium with sulfoxides having an α -proton have been well-studied [44-47]. Methylolithium and LDA mainly abstract the α -proton. *n*-Butyllithium and *t*-butyllithium, on the other hand, attack the sulfur causing a ligand exchange on the sulfoxide. Jacobus and Mislow [44] report the racemization and cleavage of optically active aryl methyl sulfoxides with methyl and phenyllithium. According to their mechanism racemization of the sulfoxide and exchange of the alkyl group takes place via a sulfine intermediate (Figure 3-5). They also proposed a sulfurane adduct to account for the exchange of the aryl group (Figure 3-6).

Durst et al. [47] have disagreed with the above mechanisms. They found two competing reactions when various sulfoxides were reacted with alkyllithiums: a) abstraction of an α -hydrogen to give α -lithio sulfoxide and b) carbon-sulfur bond cleavage according to the equation



They propose a simple $\text{S}_\text{N}2$ displacement at sulfur and considered the sulfurane as a transition state not an intermediate. In our system displacement of the phenyl group by TPML at -78°C is unlikely because TPML is less basic and more sterically hindered compared with alkyllithium. The nature of the side reaction is possibly associated with the presence of chelated stereoisomers some of which propagates faster than others. A true side reaction, therefore may not be present.

We found the polymerization of PVS to be extremely rapid even at -78°C . Thus at 25°C the polymerization is expected to be even more rapid. The two initiating or propagating species (slow and rapid) that are seen

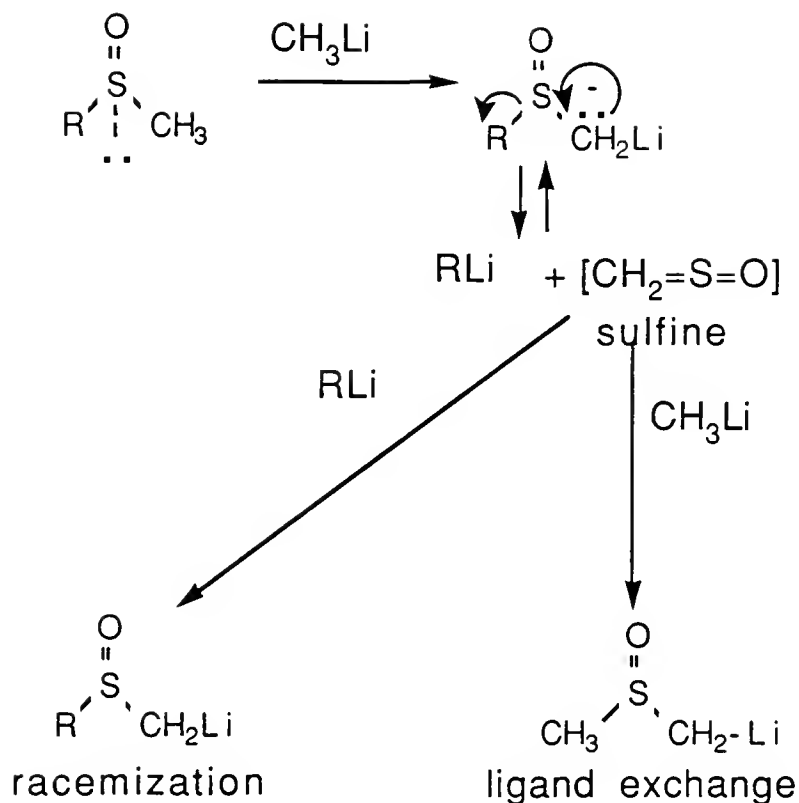


Figure 3-5. Sulfine intermediate formed during racemization of sulfoxides.

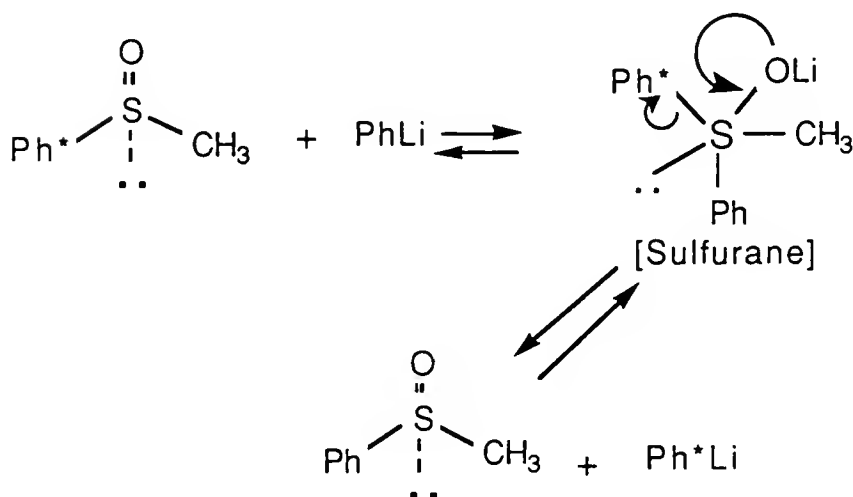


Figure 3-6. Sulfurane intermediate formed during ligand exchange in phenylmethanesulfoxide.

would be expected to form and propagate in the first few seconds of the polymerization. Thus cooling the reaction mixture after initiation at 25°C does not have much effect on the distribution and we still see the bimodal nature of the chromatogram (Figure 3-4) (Run 5 in Table 3-2).

The total absence of bimodal distributions for the samples initiated at -78°C suggests that at -78°C we form only one initiating species which propagates further. Warming the solution up to 25°C after initiating at -78°C does not give rise to bimodal distribution (Runs 6 and 7 in Table 3-2). However, the molecular weight distribution of the sample was considerably broadened when it was warmed up to 25°C. This indicates a different effect of temperature on the polymerization as compared to the initiation (see below).

Also from Table 3-2 it is seen that lower the polymerization temperature narrower the MW distribution. The difference in molecular weight distributions observed at the same temperature (-78°C) for different runs (Tables 3-1 and 3-2) for the same initiator is probably due to the difference in the purity of monomer from batch to batch. Also this small variation may be due to changes in the SEC conditions. Although all the SEC runs were carried out as much as possible under identical conditions and although the calibration curves were recalibrated from month to month there would still be the some experimental error involved with the system (i.e. change in flow rate due to wear and tear of the pump, leakage in the system, difference in the injection conditions, difference in the concentration of the solution injected, etc.).

Effect of Temperature on Polymerization

It was noticed that warming the polymerization mixture to 25°C resulted in a change in color from yellowish-green to red which

progressively became darker with time. The dark red color did not discharge when terminated with methanol. Furthermore the molecular weight distributions of the polymers were found to broaden considerably at higher temperatures (Table 3-2). This was an indication that polymerization side reactions played an important role at ambient temperatures. As mentioned before efforts to determine the colored side products by UV/VIS spectrometry failed due to the strong absorption of the sulfoxide group in UV (λ_{max} 253 nm).

The side reactions are seen to be present even at -78°C . Thus a tailing effect in the SEC chromatograms were usually observed (Figure 3-7), which was always in the low molecular weight region. The tailing and consequent worsening of the molecular weight distribution was more prominent for longer reaction times. Even at -78°C , after termination, there was usually a yellowish tinge in the solution which was not due to the living carbanions.

During the initial stages of our investigation of this system we attributed the tailing due to our inability to completely purify PVS to anionic polymerization standards. As mentioned in Chapter 2 the importance of rigorous purification of solvents and reagents during anionic polymerization cannot be overemphasized. The presence of parts per million of electrophilic impurities could be disastrous especially for the preparation of high molecular weight polymers [25, 26]. Sulfoxides are known to form strong hydrogen bonds so that hydrogen bonds may have formed with electrophiles such as water. PVS is probably synthesized from a Grignard reaction of vinyl magnesium bromide with ethylbenzenesulfinate [2]. It is conceivable that some of the reactants may

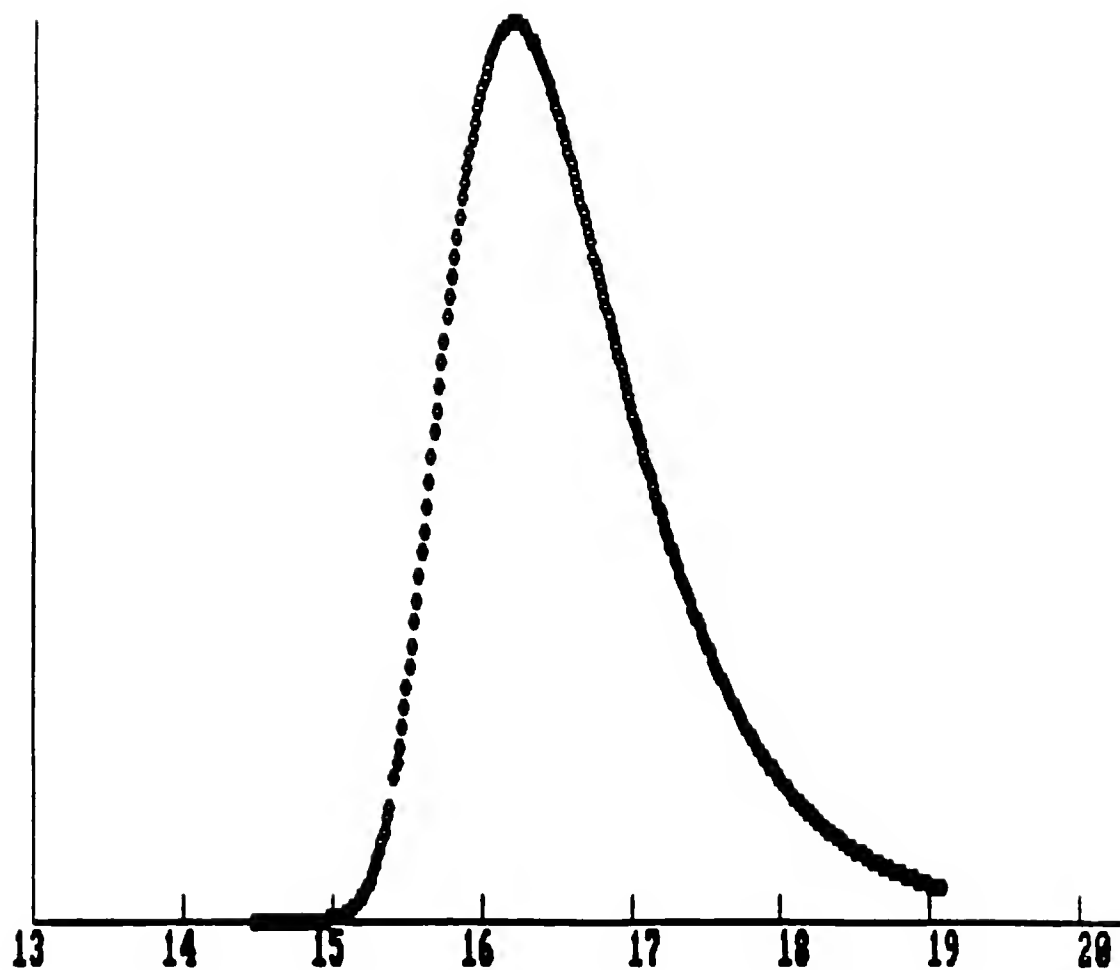


Figure 3-7. SEC chromatogram of PPVS initiated by TPML in THF at -78°C and polymerized at -78°C for 33 hours. Eluting solvent: THF. Flow rate: 1 ml/min.

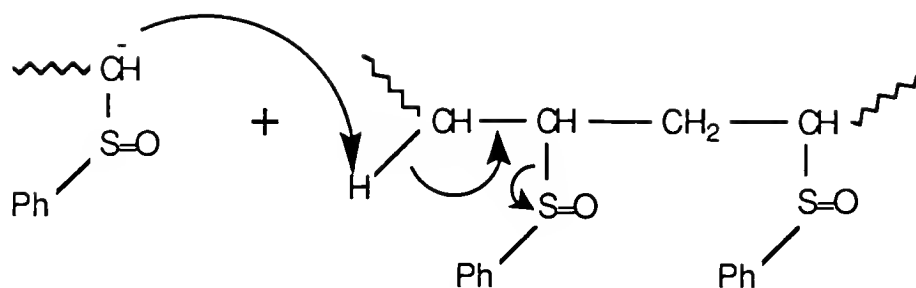
have been left behind which may have very close boiling points and thus cannot be completely removed through distillation.

Another possibility is the decomposition of the monomer during distillation at high temperatures. Mislow did extensive studies on the thermal racemization of alkyl aryl sulfoxides [52, 53]. They estimated the bond dissociation energy of cleavage of C-S bonds in alkyls and aryls to be about 56-69 kcal/mole whereas the activation energy of the pyramidal inversion was estimated to be about 36 kcal/mole [52]. Thus they discounted the homolytic cleavage-recombination mechanism for racemization except in case of benzyl p-tolylsulfoxide which gives rise to benzyl and p-toluenesulfinyl radicals upon cleavage of the benzylic C-S bond [53]. Another possibility is a five-center pyrolytic cis-elimination mechanism for sulfoxides having a β -hydrogen (Figure 3-8) [3, 54]. A detailed discussion of this elimination will be given in Chapter 4.

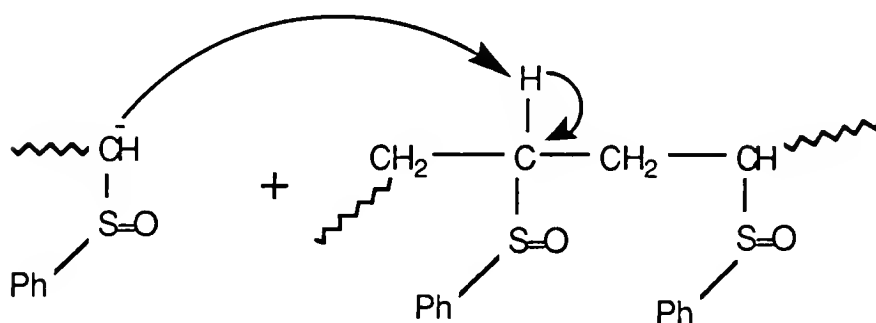
The absence of detectable impurities in GC leads us to believe that the tailing effect in the low molecular weight side in polymerizations carried out at -78°C may be due to factors other than impurities in the monomer. It was noticed that the side reactions were more prominent in polymerizations with long reaction times so that the growing polymer chain is somehow deactivated during the polymerization. Several explanations are possible since we have a number of sites in the polymer chain which could be attacked by a carbanion leading to various side products. Apparently these side reactions are strongly temperature dependent and lead to broad molecular weight distribution (Table 3-2).

Probable deactivation reactions could be

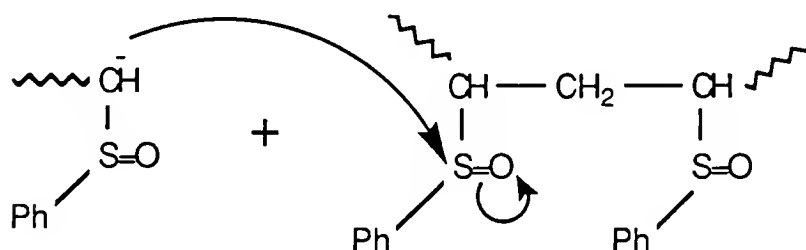
- i. E₂ elimination of phenyl sulfenic acid in the polymer chain by a growing carbanion [55, 56] to form polyene linkages in the chain



ii. Deprotonation of an α proton in the chain to form a dipole stabilized carbanion [44-48]



iii. Attack on the sulfinyl of a polymer chain by the growing α -lithio sulfoxide [47]



The pK_a of LDA [57] is very similar to that of the α -lithio sulfinyl carbanions [48]. Thus it was decided to investigate the effect of LDA on PPVS. LDA was prepared in vacuo by a reaction of diisopropyl amine and

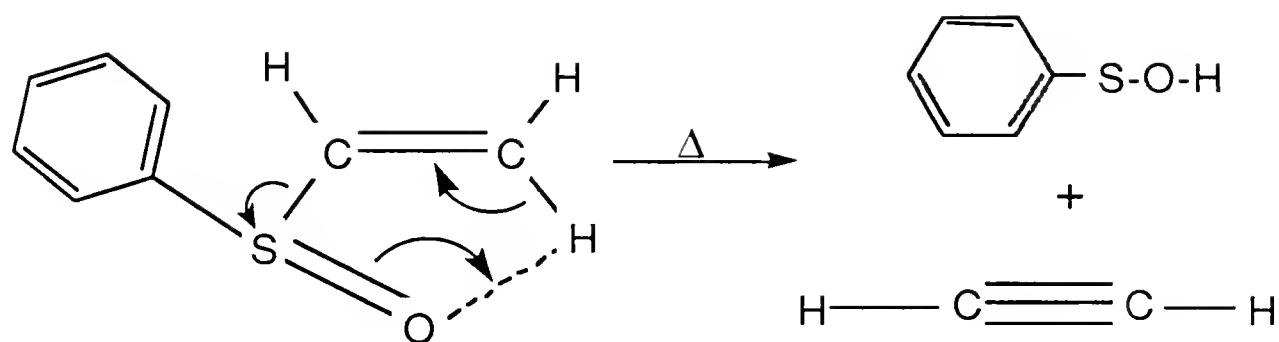


Figure 3-8. Possible elimination reaction in phenylvinylsulfoxide at high temperatures.

methylolithium. The ratio of LDA:sulfoxide was about 1:1. The THF solution of PPVS was then added to the THF solution of LDA at -78°C . It was seen that the polymer solution turned dark red (similar to that of the solution of polymerization at 25°C). After about 15 minutes methanol was added to quench any LDA left behind and the polymer was purified by precipitation in ether. The polymer was not completely soluble in THF. The SEC of the soluble polymer showed a decrease in molecular weight as compared to the starting polymer. Thus a cleavage of chains by LDA at -78°C may have occurred. The change in color upon reaction of LDA with PPVS may be due to the formation of low MW polyenes in the polymer due to a β elimination of phenyl sulfenic acid as discussed above.

Conversion of (\pm) PVS With Time

A rough idea of the conversion of monomer with time and the kinetics was highly desirable. This would give us the half life of the polymerization reaction and would help us decide when to terminate the polymerization so as to obtain reasonable yields without the side reactions associated with long reaction times.

A polymerization reaction was carried out at -78°C under rigorously dried argon and aliquots of the polymerizing solution were withdrawn by syringe at various times. Naphthalene was employed as an internal standard to monitor the concentration of the monomer at various times during polymerization (Chapter 2). The polymer was also characterized by SEC. The results of one of the runs are summarized in Table 3-3. Surprisingly the variation in molecular weight was negligible from 5 minutes to 3 hours. Also no detectable monomer was found by GC even after just a few minutes of reaction. This indicated that the polymerization of PVS was extremely rapid even at -78°C .

Table 3-3. SEC Results of the Conversion of Monomer with Time. Initiated by TPML in THF at -78°C under Argon.

TIME minutes	M_p^a SEC	M_w	M_n^b	M_w / M_n
5	5859	6559	3772	1.74
15	6215	7209	4096	1.76
60	6691	7852	4708	1.67
120	6790	7515	4001	1.88
180	6891	7907	4053	1.95

a. With reference to polystyrene standards.

b. M_n Calculated = 2854.

Since stop-flow techniques were not available, an experiment was devised wherein the polymerization reaction was terminated at incomplete conversion. The time of reaction was 21 seconds after which the polymerizing solution was quenched with methanol. The polymer was precipitated as usual in excess of ether and the concentration of monomer in the filtrate was determined by GC.

The rate constant for the pseudo-1st order polymerization reaction (at a concentration of living polymer chains of approximately 10^{-3} M) determined in this way was found to be 0.17 sec^{-1} with a half life of 4.1 seconds. Thus the polymerization reaction is seen to be extremely rapid.

Several factors must be considered before accepting the above value of the rate constant. There could be errors involved in the determination of the time of polymerization. Also the rate of polymerization may not necessarily be pseudo-1st order (i.e., the assumption that the concentration of the living ends is constant may not be true).

Polymerization and Studies of (+)-PVS

Optically active (+)-PVS $\{[\alpha]_D^{20} = 358.50\}$ was polymerized using a procedure similar to that used for the racemic monomer using TPML in THF at -78°C . The polymer shows some unique properties.

It was found that the optically active monomer does not lose its optical activity upon polymerization. This is expected since sulfoxide sulfur does not epimerize under the polymerization conditions [1, 2]. As seen from the ^{13}C NMR (Figure 3-9) all of the signals from the optically active polymer are considerably sharper than the corresponding ones of the racemic PPVS (Figure 3-10). This suggests a highly stereoregular structure of (+)-PPVS as compared to the racemic polymer. The (+)-PPVS would be expected to be isotactic as suggested by the broad methylene absorption in ^1H NMR and by the stereochemistry of the dimers and trimers studied extensively by Buese and Hogen-Esch [1, 2]. The polymer was found to be only partially soluble in THF and chloroform both of which are excellent solvents for racemic PPVS. The polymer is soluble in glacial acetic acid. The decrease in solubility of (+)-PPVS also points to a more regular structure. The polymer was found to be monodisperse ($M_n = 1359$, M_n Calculated = 2920, $M_w/M_n = 1.19$).

Copolymerization of Styrene and PVS

Both A-B and A-B-A type of copolymers were synthesized as described in the experimental section.

A-B Copolymers

Figure 3-11 illustrates the various steps in A-B block copolymerization and Table 3-4 summarizes the SEC data of various A-B copolymerizations.

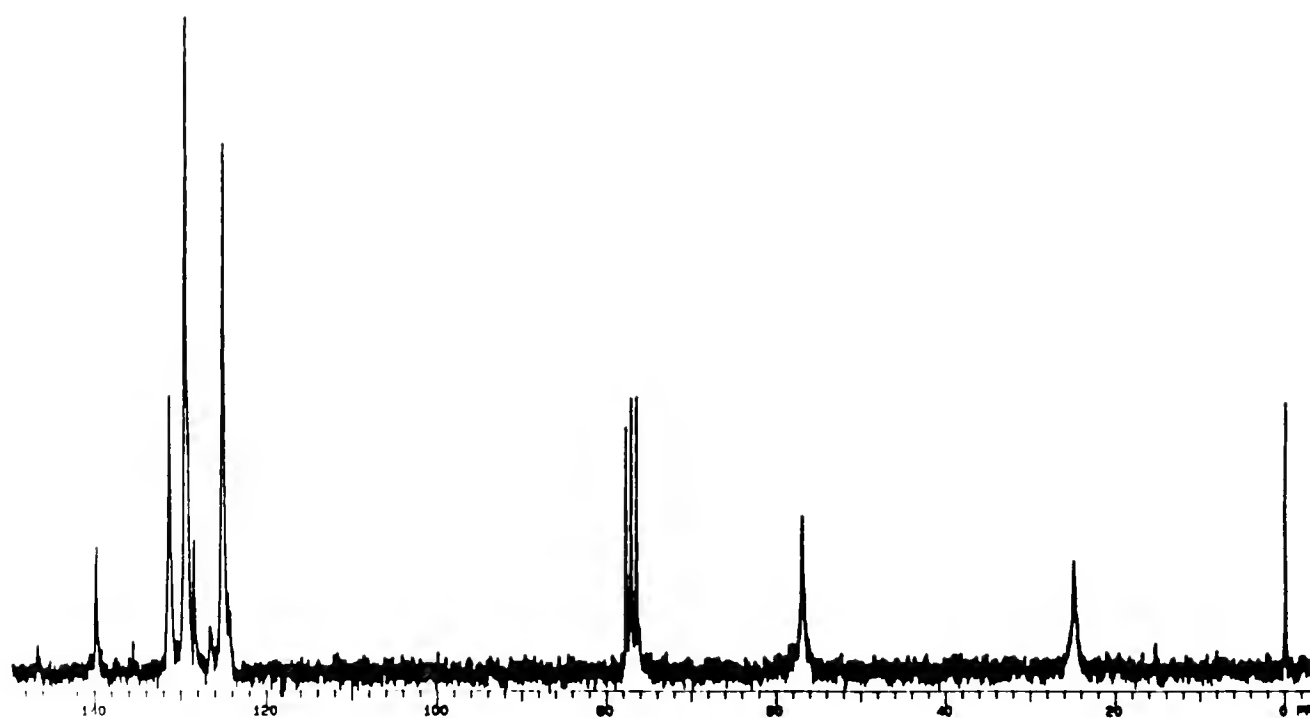


Figure 3-9. 50 MHz ^{13}C NMR of (+)-PPVS in CDCl_3 at room temperature.

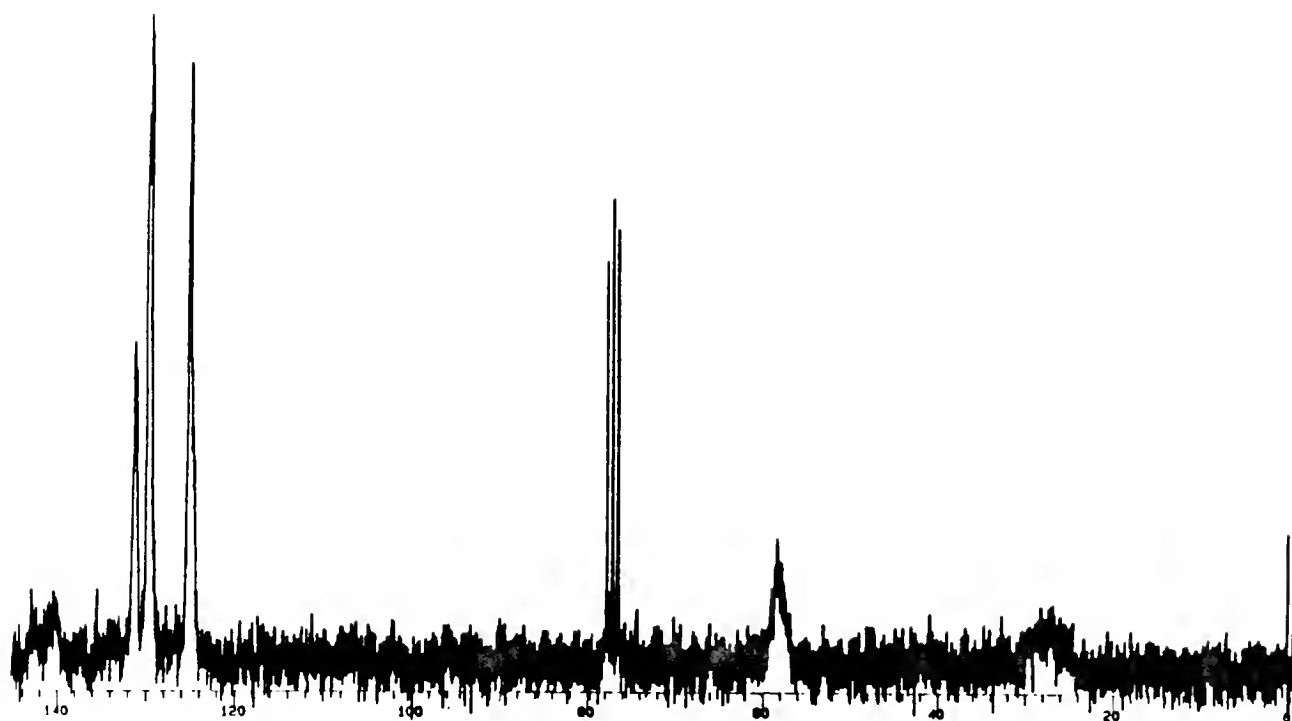


Figure 3-10. 50 MHz ^{13}C NMR of racemic PPVS in CDCl_3 at room temperature.

Table 3-4. A-B Diblock Copolymerization of Styrene and PVS in THF at -78°C

Sample	Moles Styrene $\times 10^{-3}$	Polystyrene Block		Moles DPPL ^b $\times 10^{-3}$	Moles PVS Added $\times 10^{-3}$	AB Diblock		Yield % ^e	PPVS % ^f
		M _n Calc'd ^a	M _p SEC			M _n Calc'd ^c	M _p SEC ^d		
AB21	8.76	3,432	2,713	0.360	2.25	3,664	3,979	98.6	21.32
AB53	6.13	3,432	2,713	0.250	6.75	6,790	7,954	97.0	47.08
AB66	7.00	3,432	2,713	0.288	14.30	10,271	11,245	96.9	66.82
AB85	6.13	3,432	2,713	0.252	35.00	16,920	17,101	68.1	74.85
AB90	1.93	3,432	2,713	0.079	15.80	19,055	19,252	54.3	78.37
PSPVS	28.40	8,687	9118	0.250	23.00	16,647	13,120	56.2	47.42
ABd89	10.00	2,359	3,341	0.440	2.25	4,121	3,733	95.6	--

a. M_n Calculated = moles styrene / moles t-butyllithium $\times 104$.

b. DDPL = Polystyryllithium capped with DPE. Measured by UV/Vis.

c. M_n Calculated = moles PVS converted / moles DPPL $\times 152.22$ + M_n polystyrene block.

d. M_p SEC with reference to polystyrene standards.

e. % Yield = gs of polymer / gs of monomer $\times 100$.

f. % PPVS calculated from the ratio of aromatic absorptions of sulfoxide phenyl ($\delta=7.4$ PPM) and polystyrene phenyl ($\delta=7.0$ PPM {meta and para protons} and $\delta=6.5$ PPM {ortho protons}).

g. Diblock using styrene-d8.

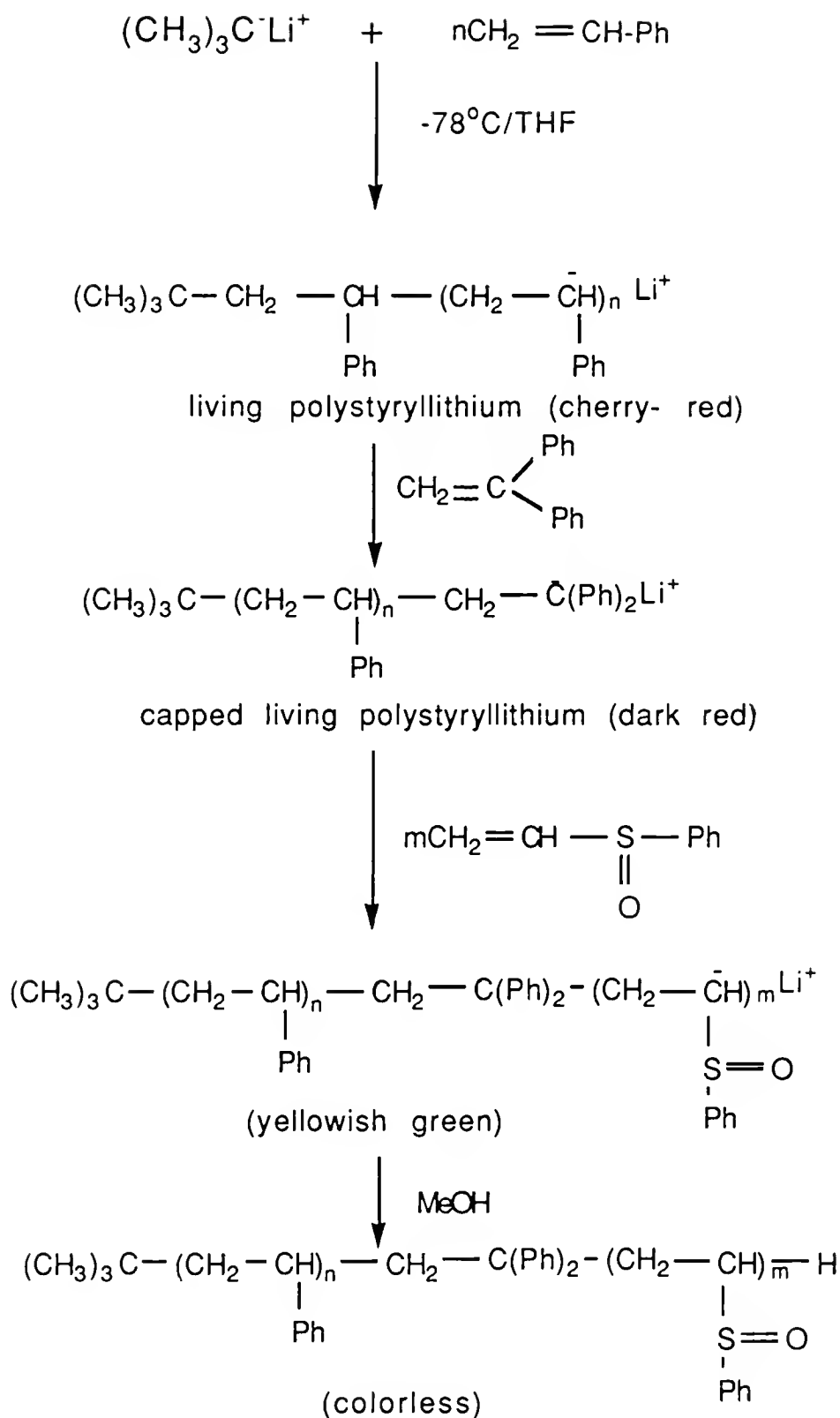


Figure 3-11. A-B copolymerization of styrene and PVS.

Styrene was polymerized by a slow vapor phase addition of the monomer onto a rapidly stirred initiator solution at -78°C in vacuo [25, 26]. Several initiators like methyllithium, s-butyllithium, etc. were tried. However we found purified t-butyllithium to be the most efficient. This initiator gave polymers with reproducible molecular weights and narrow molecular weight distributions.

As can be seen from Table 3-4 the M_n calculated from the concentrations of monomer and initiator (determined by UV) was quite close to the one determined by SEC. Also the molecular weight distribution for the styrene block was narrow (<1.1) which indicates negligible killing of the growing polystyryllithium chains. Thus the DPE capped polystyryllithium was seen to be an excellent initiator for PVS. The molecular weight distributions were also better than for homopolymers of PVS which is expected since we start out with polymeric initiators of narrow molecular weight distribution. However at high PVS concentrations considerable termination during polymerization was observed as seen from the worsening molecular weight distribution and lower yields (entries 4 and 5 in Table 3-4).

Figure 3-12 shows a typical SEC chromatogram of the polystyrene homopolymer (i) and styrene-PVS copolymer (ii). The PPVS content in the copolymer was calculated from the ^1H aromatic absorptions of the polystyrene phenyls ($\delta = 7.0$ PPM {meta and para} and $\delta = 6.5$ PPM {ortho}) and the sulfoxide phenyls ($\delta = 7.5$ PPM). Figure 3-13 is a 200 MHz ^1H NMR of a styrene-PVS A-B diblock copolymer and Figure 3-14 is the corresponding 200 MHz ^1H NMR of poly(phenylvinylsulfoxide) initiated by TPML in THF at -78°C . The ortho protons in polystyrene are seen to be

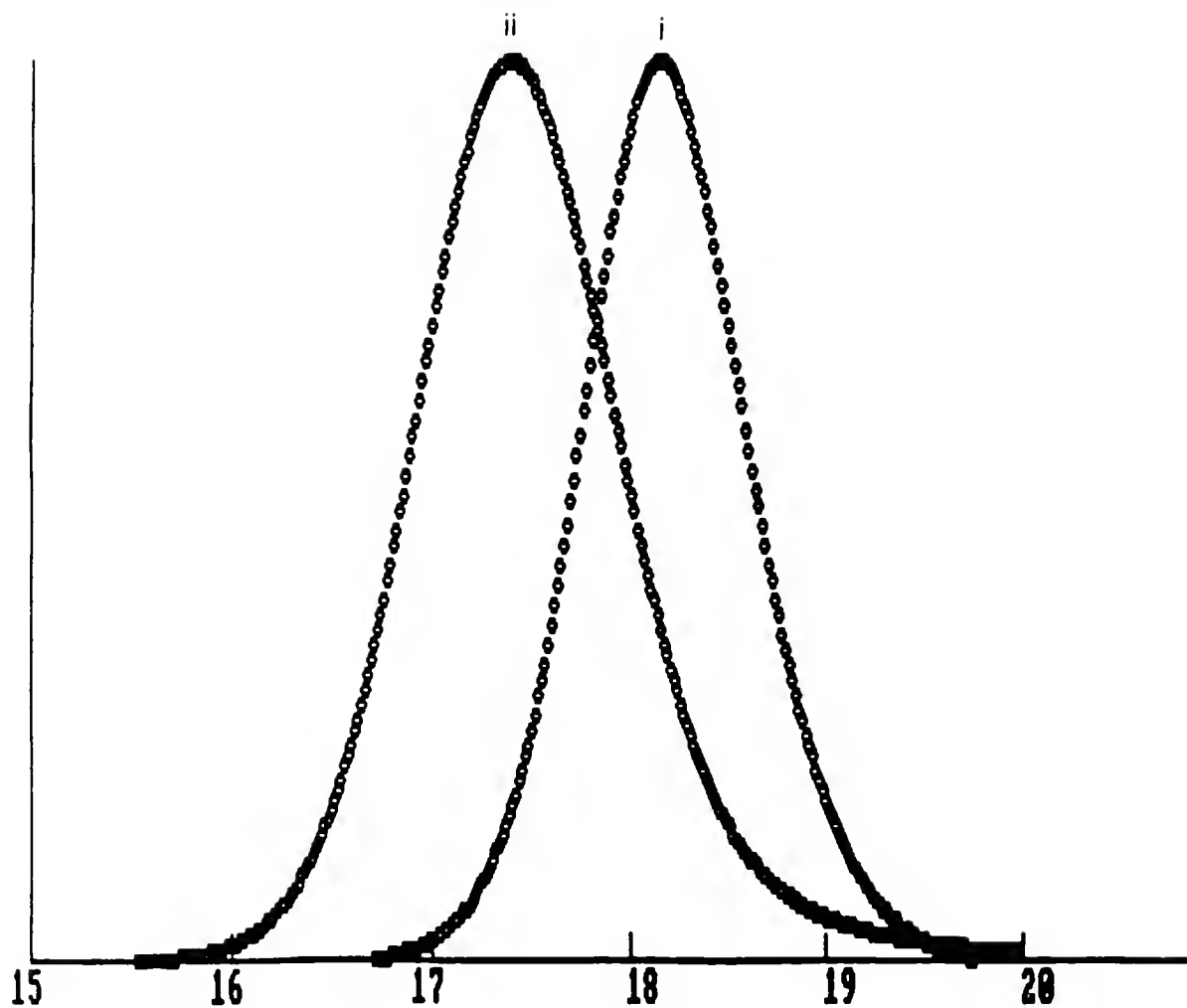


Figure 3-12. SEC chromatograms of i) Polystyrene homopolymer ($M_p = 8200$, $M_w/M_n = 1.09$) and ii) A-B copolymer of styrene and PVS ($M_p = 13,120$, $M_w/M_n = 1.09$). Eluting solvent: THF at 1 ml/min.

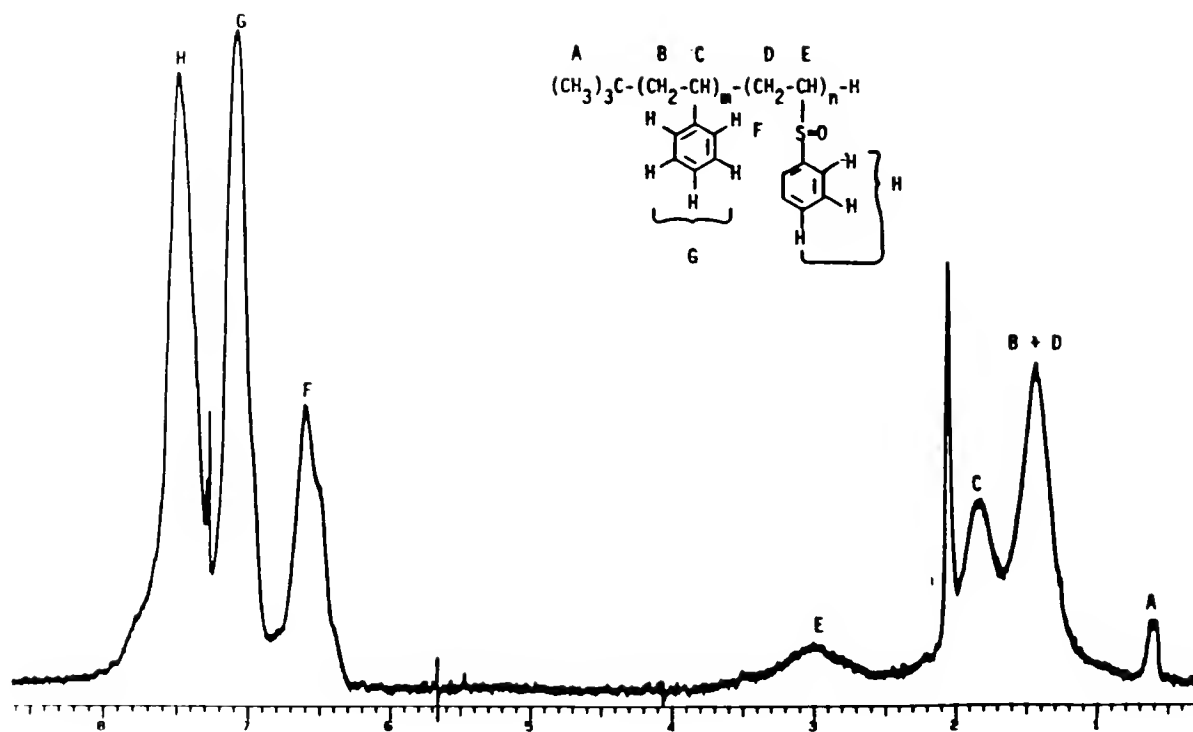


Figure 3-13. 200 MHz ^1H NMR of poly(styrene-b-PVS) copolymer in CDCl_3 at room temperature.

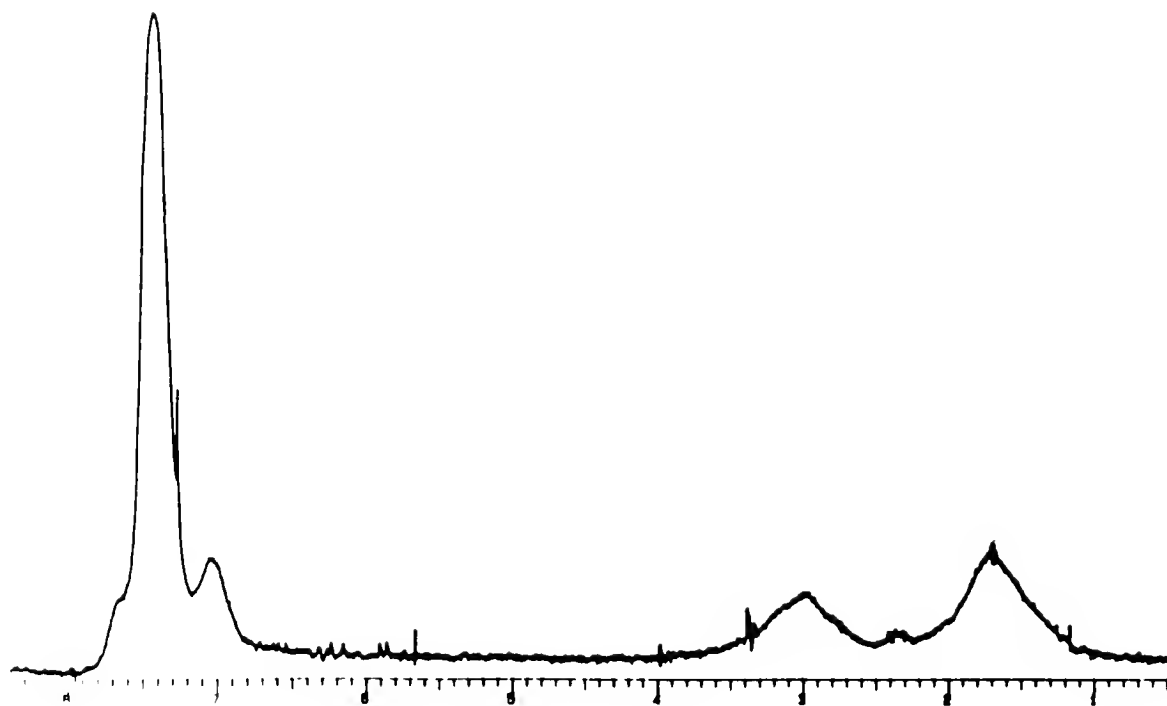


Figure 3-14. 200 MHz ^1H NMR of PPVS (initiated by TPML in THF at -78°C) in CDCl_3 at room temperature.

shifted upfield relative to the meta and para. This is due to the shielding of the ortho protons being in the anisotropic field of the π -electron current of the neighboring ring [58].

In the runs 1-5 the polystyrene block was kept constant (M_p SEC = 2,713) whereas the sulfoxide content was varied. There was a good correlation between the sulfoxide content calculated (from the ratio of moles of styrene to moles of PVS) (21%, 53% and 66%) and that observed from ^1H NMR (21%, 47% and 67% respectively) for the first three runs. However, a large variation was seen for runs 4 and 5 (85% and 90% calculated and 75% and 78% observed). This also indicates substantial killing during runs 4 and 5, where the concentration of PVS was high.

Run 7 was carried out using styrene- d_8 and the corresponding copolymer was used for the structure determination of the thermal elimination product.

A-B-A Copolymers

Figure 3-15 illustrates the various steps in the A-B-A block copolymerization and Table 3-5 summarizes the SEC data of the A-B-A runs.

Lithium naphthalide was employed as the initiator for the two-ended polymerization of styrene [39]. As is well known [25, 26] lithium naphthalide initiates polymerization of styrene by electron transfer to form the radical anion of the monomer which then immediately couples and forms the dimer with two anions on either end. This dimer can further propagate in both directions to give a two-ended polystyryllithium.

Excellent results were obtained when lithium naphthalide was prepared using excess of naphthalene (Table 3-5) (Figure 3-16). However, when lithium naphthalide was prepared by using an excess of lithium metal

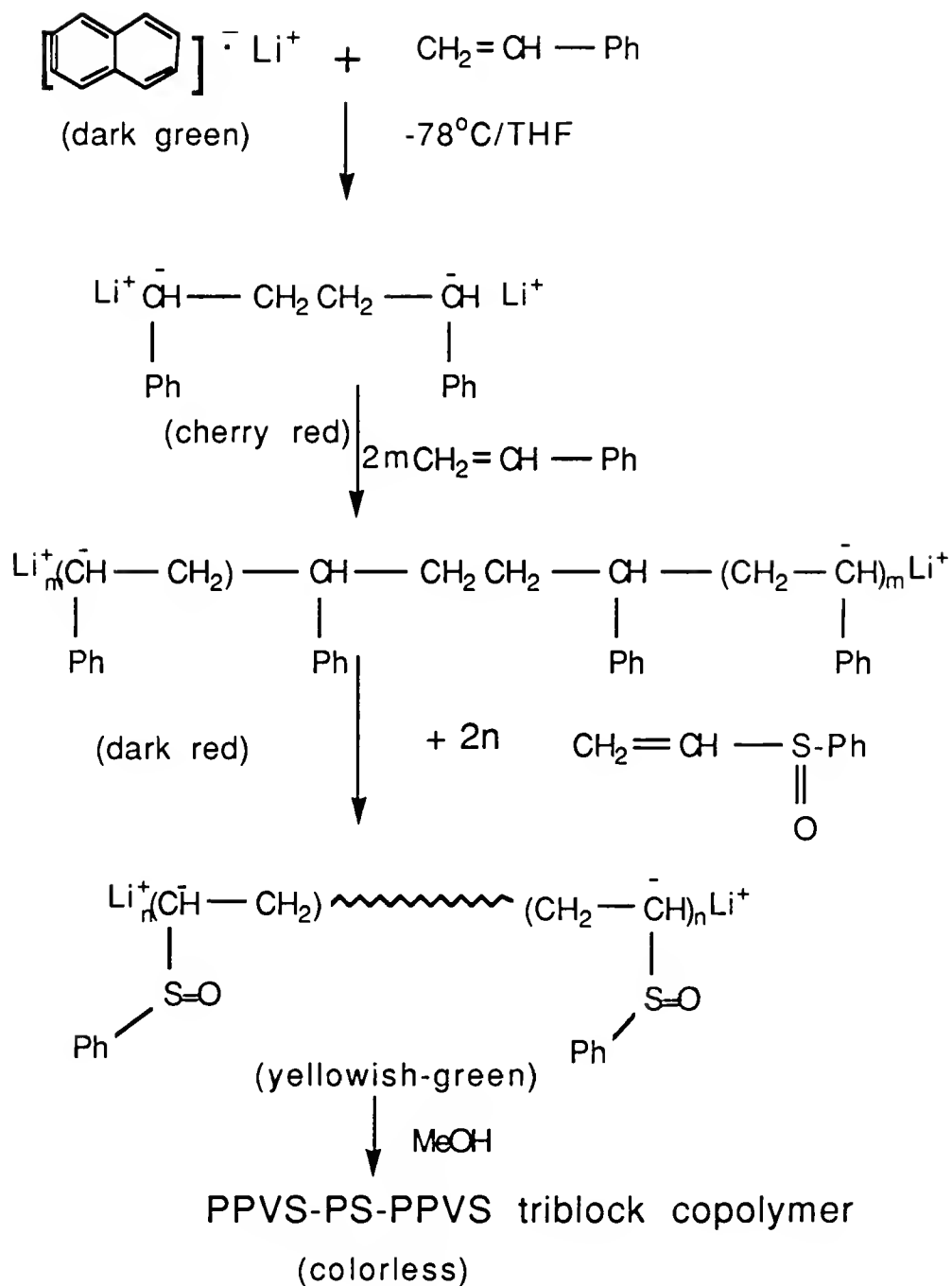


Figure 3-15. A-B-A copolymerization of styrene and PVS.

Table 3-5. A-B-A triblock copolymerization of Styrene and PVS in THF at -78°C

Sample	Moles Styrene x10 ⁻³	Polystyrene Block			Moles DDPPL ^b x10 ⁻³	Moles PVS Added x10 ⁻³	A-B-A Triblock			Yield % ^e	PPVS % ^f
		M _n Calc'd ^a	M _p SEC	M _w /M _n			M _n Calc'd ^c	M _p SEC ^d	M _w /M _n		
ABA30	6.35	11,960	11,393	1.07	0.132	2.7	14,506	18,152	1.14	97.9	41.80
ABA50	6.10	11,960	11,393	1.07	0.127	6.1	18,668	21,201	1.23	96.6	49.86
ABA78	5.55	11,960	11,393	1.07	0.116	19.7	29,967	30,601	1.33	74.3	65.50
ABA90	2.96	11,960	11,393	1.07	0.062	26.0	33,357	28,117	1.51	35.4	69.79
ABAS0	19.0	55,000	59,520	1.08	0.079	15.0	79,233	79,060	1.12	90.5	29.46
ABAS1	25.0	26,666	29,750	1.04	0.169	15.0	43,672	48,078	1.10	98.2	35.53
ABAd89	9.60	9,793	10,553	1.08	0.188	3.8	13,597	14,921	1.10	95.0	--

a. M_n Calculated = moles styrene / moles lithium naphthalide x 2 x 104.

b. DDPPL = Dianion of DPE capped polystyryllithium. Concentration measured by UV/Vis.

c. M_n Calculated = moles PVS converted / moles DDPPL x 152.22 + M_n polystyrene block.

d. M_p SEC with reference to polystyrene standards.

e. % Yield = gs of polymer / gs of monomer x 100.

f. % PPVS calculated from the ratio of aromatic absorptions of sulfoxide phenyl ($\delta=7.4$ PPM) and polystyrene phenyl ($\delta=7.0$ PPM {meta and para protons} and $\delta=6.5$ PPM{ortho protons}).

g. Triblock using styrene-d8.

we ended up with a bimodal distribution in the SEC chromatogram (Figure 3-17). When lithium naphthalide is prepared using excess of lithium metal one also gets the formation of naphthalene dianion alongwith the radical anion [31]. The dianion itself may initiate styrene and a naphthalene group may thus be incorporated in the middle of the chain [59]. In absence of more extensive experimental evidence we will not attempt to interpret in detail these anomalous results.

Table 3-5 once again shows that the dianion of polystyryllithium is an excellent initiator for PVS. Again the molecular weight distribution of the copolymer increases with increasing content of sulfoxide. This indicates some termination when larger amounts of PVS are used.

Proof of Dianion Formation in the Lithium Naphthalide Initiated Polystyryllithium

The "two-endedness" of the DPE capped living polystyryllithium initiated by lithium naphthalide was proved in the following manner. Styrene was independently initiated by lithium naphthalide in THF at -78°C and capped with 1,1-DPE. The concentration of the carbanions was measured using UV/VIS spectrometry (Table 3-6). The carbanion solution was attached to an apparatus equipped with a quartz cell and a quartz spacer. An excess of fluorene in a break-seal was also attached to the apparatus. This was then evacuated and the carbanion solution was poured in the cell through the break-seal and the absorbance of the red carbanion solution was measured at its λ_{max} (500 nm, Table 3-6). The living carbanion was then reacted with fluorene. An immediate change in the color of the solution was noticed on formation of the fluorenyllithium from dark red to yellow. The absorbance of the solution of fluorenyllithium was measured at its λ_{max} (373 nm) (Table 3-6). The extinction coefficient of

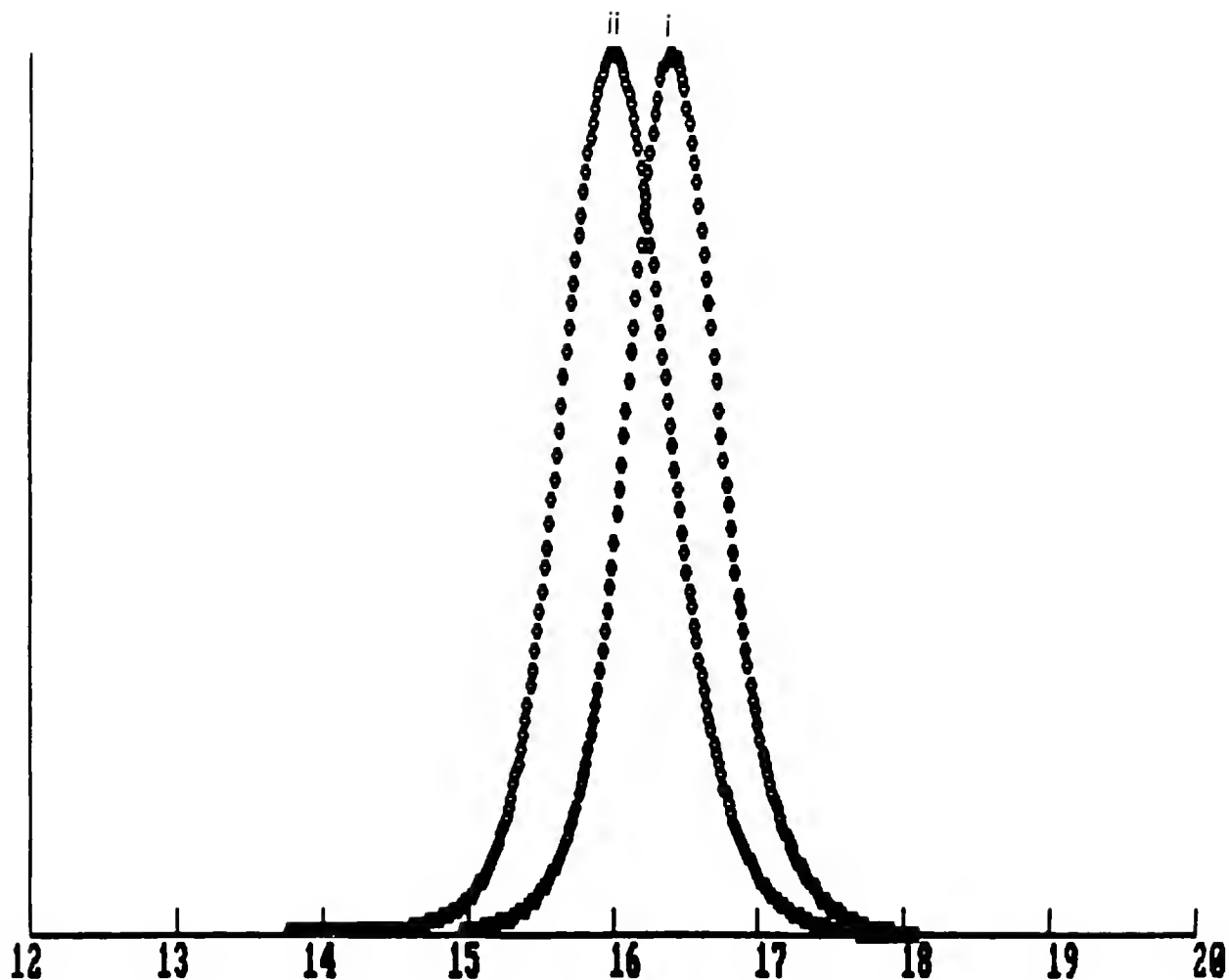


Figure 3-16. SEC chromatograms of i) Polystyrene homopolymer ($M_p = 10,553$, $M_w/M_n = 1.08$) and ii) A-B-A copolymer of styrene and PVS ($M_p = 14,921$, $M_w/M_n = 1.1$). Polystyrene block initiated by lithium naphthalide prepared by using an excess of naphthalene. Eluting solvent: THF at 1 ml/min.

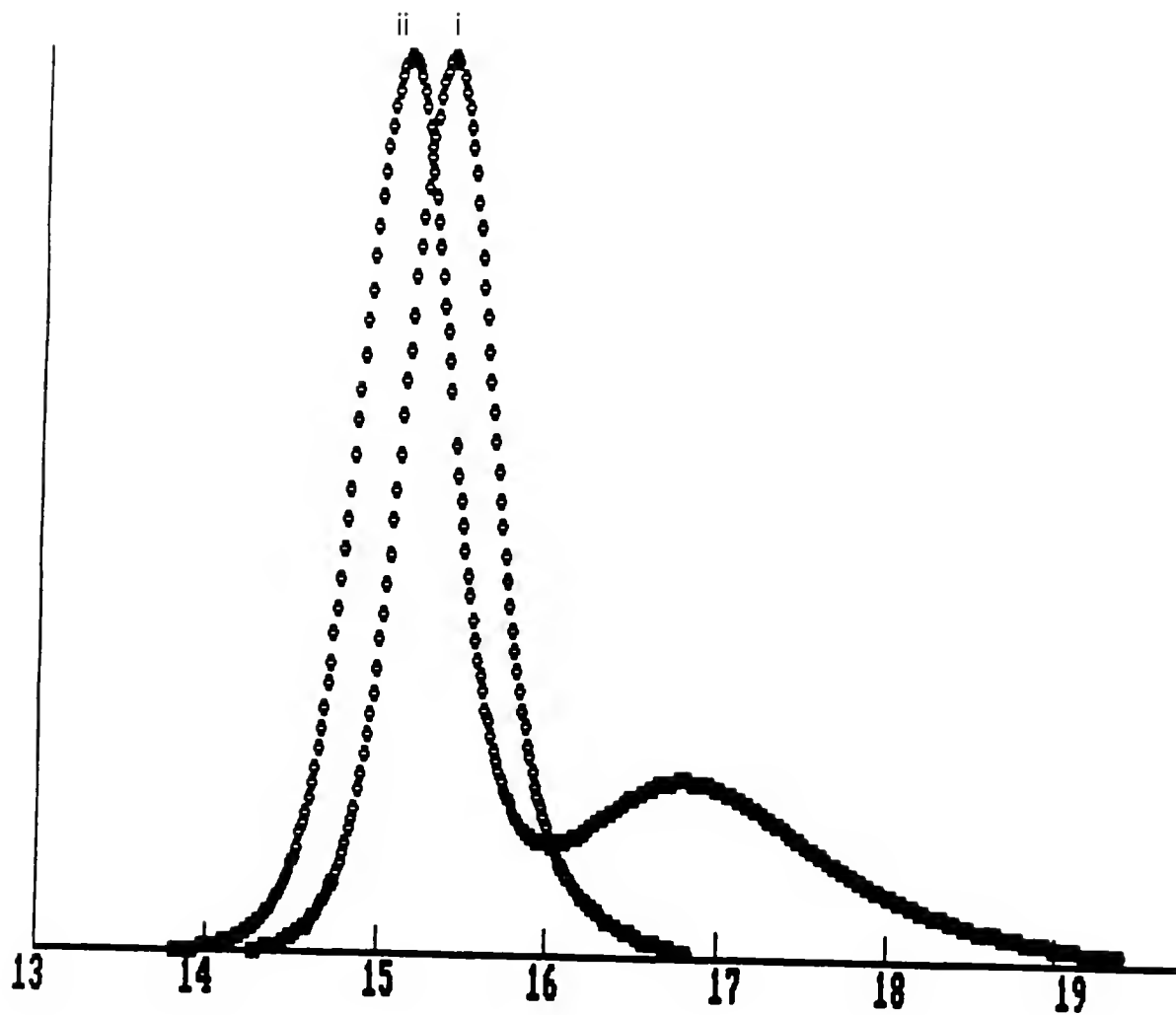


Figure 3-17. SEC chromatograms of i) Polystyrene homopolymer and ii) A-B-A copolymer of styrene and PVS. Polystyrene block initiated by lithium naphthalide prepared by using an excess of lithium metal. Eluting solvent: THF at 1 ml/min.

Table 3-6. UV/Visible data for various carbanion initiators in THF at 25°C.

CARBANIONS	λ_{MAX} nm	MOLAR EXTINCTION COEFFICIENT (ϵ)
TPML	500	30,980
TPMK	486	26,420
Lithium Naphthalide	367	10,263
	326	22,350
	292	32,550
$\alpha\text{MS-2Li}^+$	342	19,700
Polystyryllithium capped with 1,1-DPE, dianion	501	56,000
Fluorenyllithium ^a	373	9,600
Fluorenylpotassium ^b	362	11,500
Potassium Chromate ^a	372	4815

a. From references 35-37.

b. Estimated from ϵ of fluorenylsodium (λ_{max} 356 nm) = 10,800 and fluorenylcesium (λ_{max} 364 nm) = 12,000 [37].

the carbanion was thus calculated (ϵ at $\lambda_{\text{max}} = 28,000$) from that of fluorenyllithium which is well-known (ϵ at $\lambda_{\text{max}} = 9,600$) [35-37]. Hence the concentration of the dianion of diphenyl polystyryllithium was determined (moles of the carbanion solution = 3.03×10^{-6}).

The terminated polystyrene was purified by precipitation in excess of methanol and injected in SEC ($M_w = 9199$, $M_n = 8633$, $M_w/M_n = 1.07$, M_n calculated = 9591). The polymer was weighed and hence the number of moles of polymer was calculated from M_n (Moles of polymer = 1.48×10^{-4} moles.). Thus the ratio of moles of carbanion / moles of polymer was found to be 2.05. This confirms that there are two moles of carbanion for every mole of the polymer (i.e., two carbanions per growing polymer chain).

In conclusion, it is seen that homo- and copolymerization of PVS can be carried out using conventional anionic polymerization techniques. A variety of initiators could be employed but it was seen that delocalized carbanions like TPML are excellent initiators. Electron transfer initiators could also be employed to achieve two ended polymerization of PVS. There was an excellent correlation between the calculated M_n and the experimental M_n determined by SEC and ^1H NMR. The molecular weight distribution in most homopolymers was found to be narrow (≤ 1.4). The effect of temperature on initiation and propagation was seen to be dramatic. In general lower temperatures resulted in well-defined and narrow molecular weight distribution polymers. Initiation at -78°C led to unimodal distribution indicating one initiating species whereas initiation at 25°C led to a bimodal distribution due to the possible presence of two initiating species. The polymerization of (\pm)-PVS was seen to be extremely rapid with a pseudo-first order rate constant of 0.17 sec^{-1} and

a half-life of 4.1 seconds. Optically active (+)-PVS was also polymerized and the resulting polymer was found to be stereoregular in structure.

Both A-B and A-B-A block copolymers of styrene and PVS were synthesized. The A-B diblock copolymerization was carried out by vapor-phase polymerization of styrene in THF at -78°C using *t*-butyllithium as initiator followed by capping with 1,1-DPE. The capped polystyryllithium was used for initiation of the PVS block. The A-B-A triblock copolymerization was carried out by reacting two-ended polystyrene prepared by using lithium naphthalide as initiator with 1,1-DPE to give a capped stable living dianion of polystyryllithium which initiated PVS at both ends to give an A-B-A triblock copolymer, polystyrene being the inner block. The molecular weight distributions of the block copolymers were, in general, narrower than the homopolymers.

CHAPTER 4

THERMAL ELIMINATION STUDIES

The thermal instability of sulfoxides has been recognized for more than a century [60]. However, the synthetic utility of sulfoxides in organic chemistry and the detailed mechanism of elimination of sulfoxides was pioneered by Kingsbury and Cram [3]. They demonstrated the facile elimination of phenyl sulfenic acid from 1,2-diphenyl-1-phenylsulfinylpropane to give the isomeric 1,2-diphenylpropene. The mechanism they proposed involved a stereospecific cis elimination similar to the E_i Cope elimination in amine oxides [61] and elimination in selenoxides [62].

Mechanism of Sulfoxide Elimination

The mechanism of sulfoxide elimination proposed by Kingsbury and Cram [3] is accepted even today. The mechanism they proposed is similar to the classical mechanism for the internal elimination reaction. The leaving group (Ph-S-O) abstracts a hydrogen from the β-carbon (Figure 4-1). The elimination is stereospecific; the erythro (1R, 2R or 1S, 2S) sulfoxide gives trans-1,2-diphenylpropene whereas the threo (1S, 2R or 1R, 2S) gives cis-1,2-diphenylpropene at least at low temperatures.

At higher temperatures the reaction is less stereospecific. Thus at higher temperatures a C-S homolytic bond cleavage was proposed to form a sulfinyl and a benzyl radical pair without the radicals ever leaving the solvent cage [3] (Figure 4-2). Other workers in this field [7, 65, 66, 67] have accepted the above mechanism with some changes. Block [77]

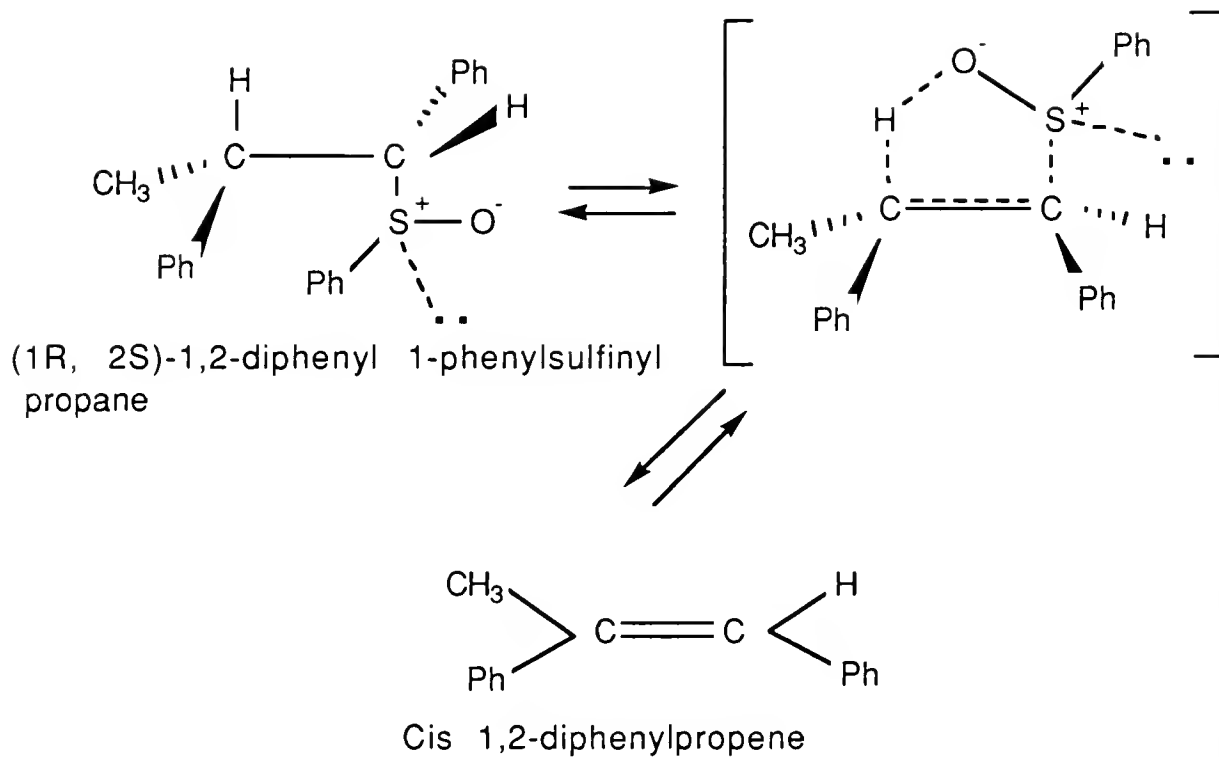


Figure 4-1. Thermal eliminations in (1R, 2S)-1,2 -diphenyl 1-phenylsulfinyl propane at low temperatures.

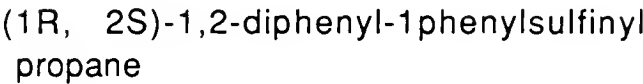


Figure 4-2. Thermal eliminations in (1R, 2S)-1,2-diphenyl 1-phenylsulfinylpropane at high temperatures.

considered the sulfoxide elimination analogous to that of the amine oxides, involving a five-membered six-electron transition state (4 electrons from the C-S and C-H σ bonds and 2 electrons as a lone pair on oxygen) and termed it as a $\sigma^2s + \sigma^2s + \omega^2s$ sigmatropic elimination.

Kwart et al. [54] carried out a detailed comparison of the sulfoxide and amine oxide thermolysis. A temperature dependence of the kinetic deuterium isotope effect was found for the deuterated sulfoxides. This result was apparently in keeping with what has been established for a planar, concerted, pericyclic transition state. In contrast the amine oxide elimination was indicative of a bent, cyclic transition state.

Use of Sulfoxides as Acetylene Synthons

Vinyl sulfoxides have been extensively used in synthetic organic chemistry as acetylene equivalents. It would serve us well to know a little about the synthetic value of sulfoxides to introduce a vinyl group in a molecule.

Michael Addition-Elimination.

Vinyl sulfoxides react with certain nucleophiles to give Michael-type addition [4-9]. This Michael-adduct could then be subjected to thermolysis to introduce a vinyl group. Thus vinyl sulfoxides were shown to be acetylene synthons in Michael addition. This is illustrated in Figure 4-3 [4, 5] and Figure 4-4 [6]. The Michael adduct could also be subjected to reductive desulfurization [9].

Alkylation-Elimination.

Trost [63, 69] carried out a series of synthetic reactions involving the alkylation of α -sulfinyl carbanions and eliminations of the resulting sulfoxides to give α - β unsaturated olefins (Figure 4-5).

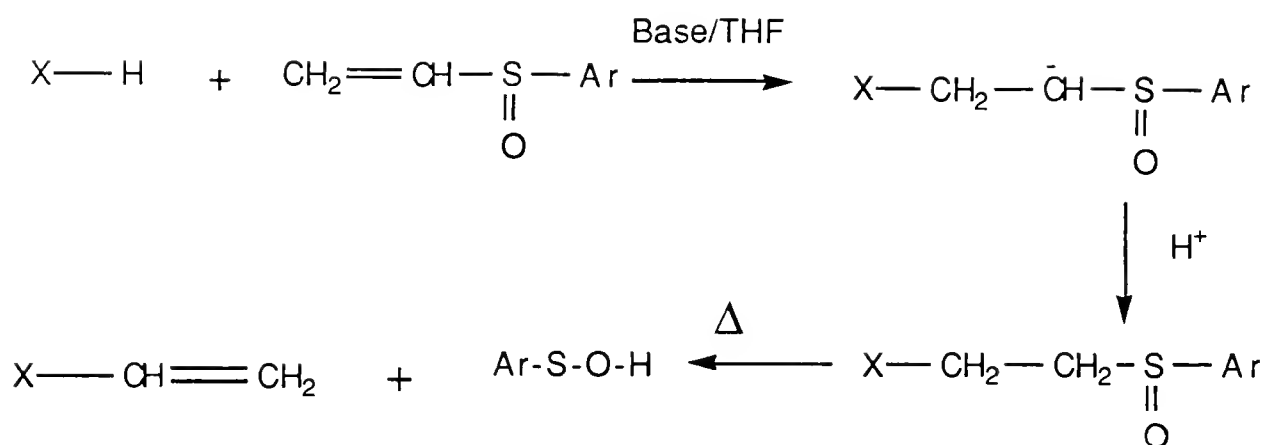


Figure 4-3. Michael addition-elimination of vinyl sulfoxides.

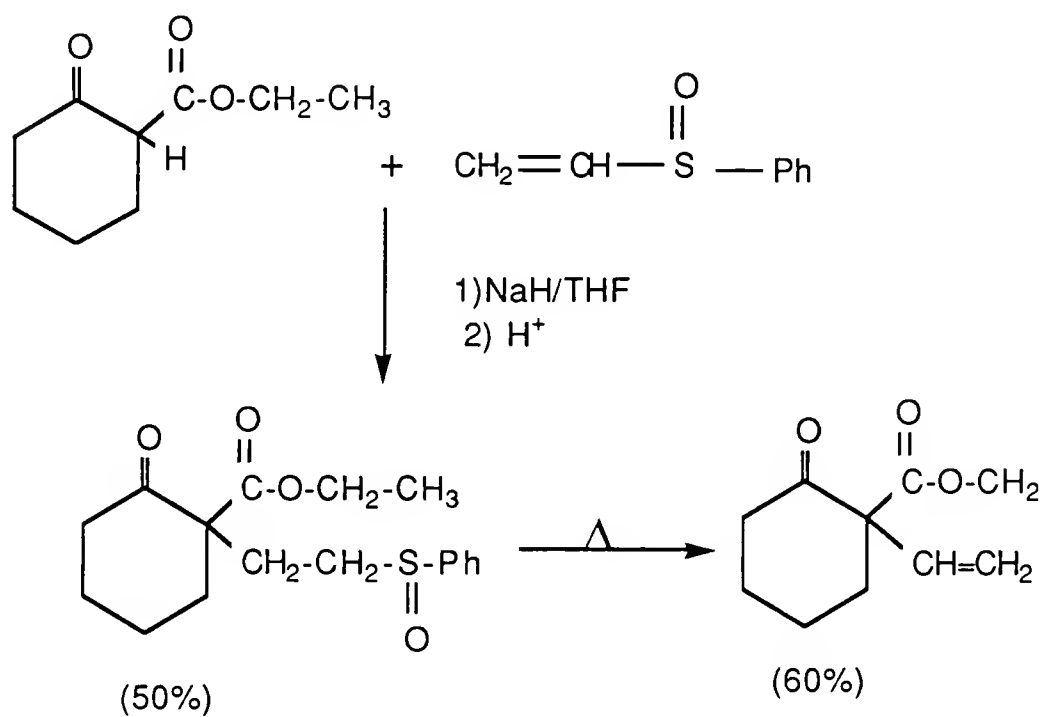


Figure 4-4. PVS as a vinyl synthon.

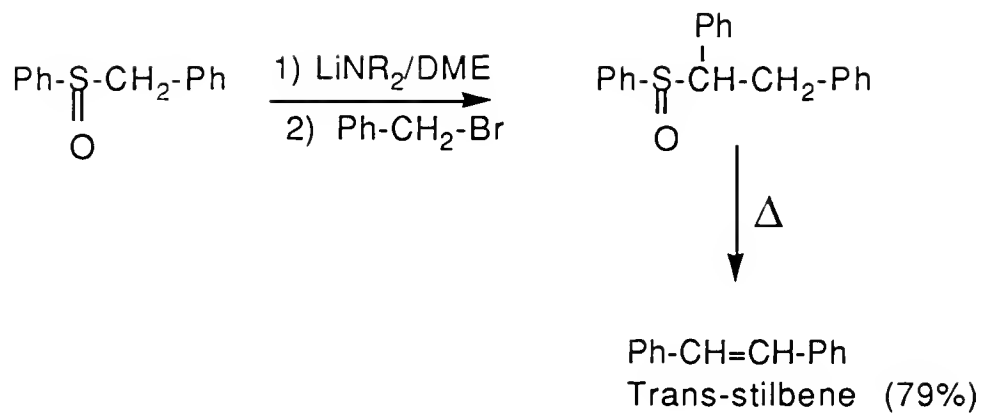


Figure 4-5. Alkylative eliminations.

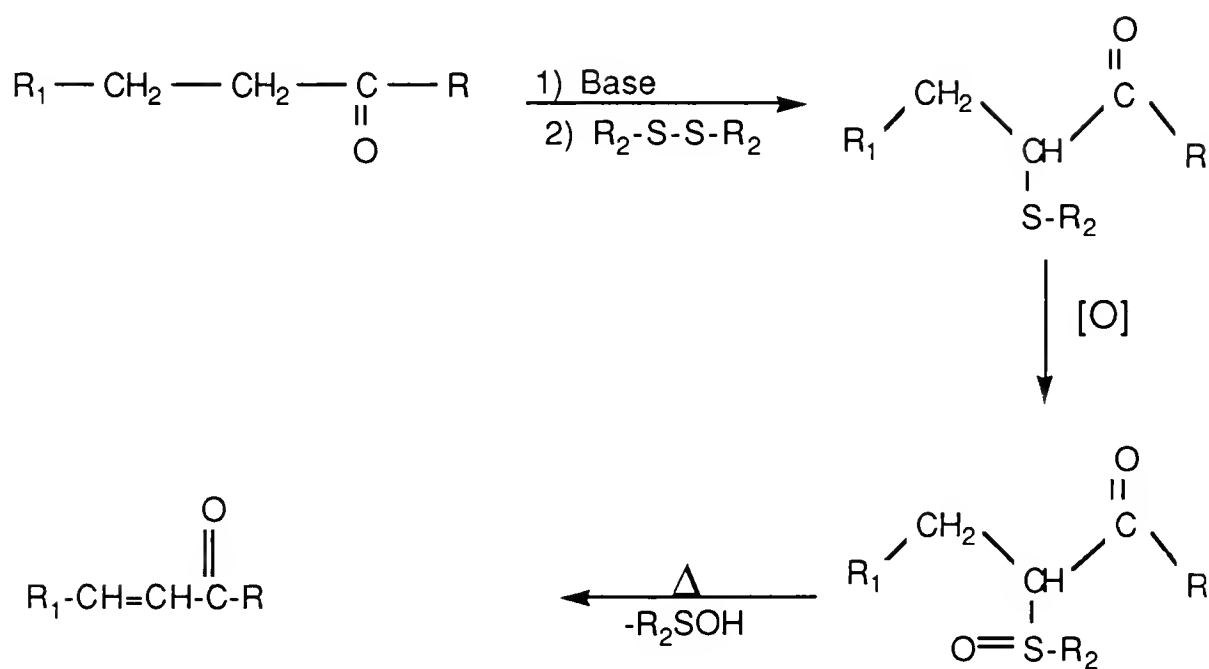


Figure 4-6. Sulfenylation-dehydrosulfenylation route to unsaturated ketones and esters.

Sulfenylation-Dehydrosulfenylation.

Trost [64-65] utilized the facile elimination of R-S-OH from sulfoxides to introduce unsaturation α,β to a carbonyl group. A general scheme for their approach of sulfenylation of ester and ketone enolates and the oxidation and thermal elimination of the resulting sulfides is shown in Figure 4-6.

Diels-Alder Cycloadditions and Elimination

Paquette et al. [10] used PVS as an acetylene equivalent in Diels-Alder cycloadditions. They utilized the dienophilicity of PVS and the in situ thermal extrusion of phenyl sulfenic acid to give a one-pot reaction giving the product of an acetylene-like Diels-Alder cycloaddition (Figure 4-7).

1.3 Dipolar Cycloaddition and Elimination

Matsumoto et al. [68] used the above Diels-Alder reaction in 1,3 dipolar cycloadditions of PVS to dicyanomethylids. Thermal elimination of the adducts gave 3-cyanoindolizines in moderate to good yields (Figure 4-8) indicating the use of PVS as an acetylene synthon in 1,3-dipolar cycloadditions.

Elimination of PPVS and PS-PPVS Copolymers

Thermal elimination of the homo- and copolymers was carried out in the solid state as described in Chapter 2. The polymer was dissolved in chloroform or THF and a thin film of the polymer was cast in the pyrolysis tube by a combination of vacuum and slow rotation on the rotovap. The tube was then inserted in the furnace and the elimination carried out at 190-200°C under high vacuum (10^{-6} Torr) for 1.5 to 2.0 hours. The yellowish-white polymer became shiny black upon elimination and was handled under argon at all times.

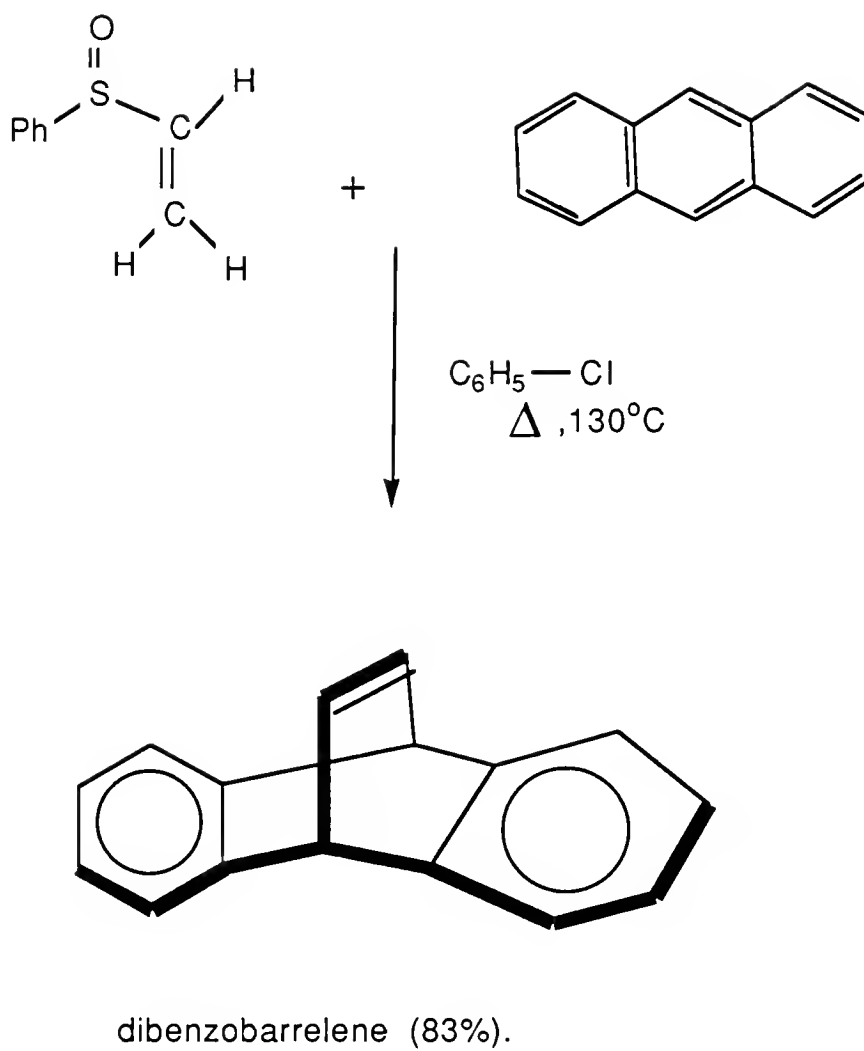


Figure 4-7. Use of PVS as an acetylene equivalent in Diels-Alder cycloadditions.

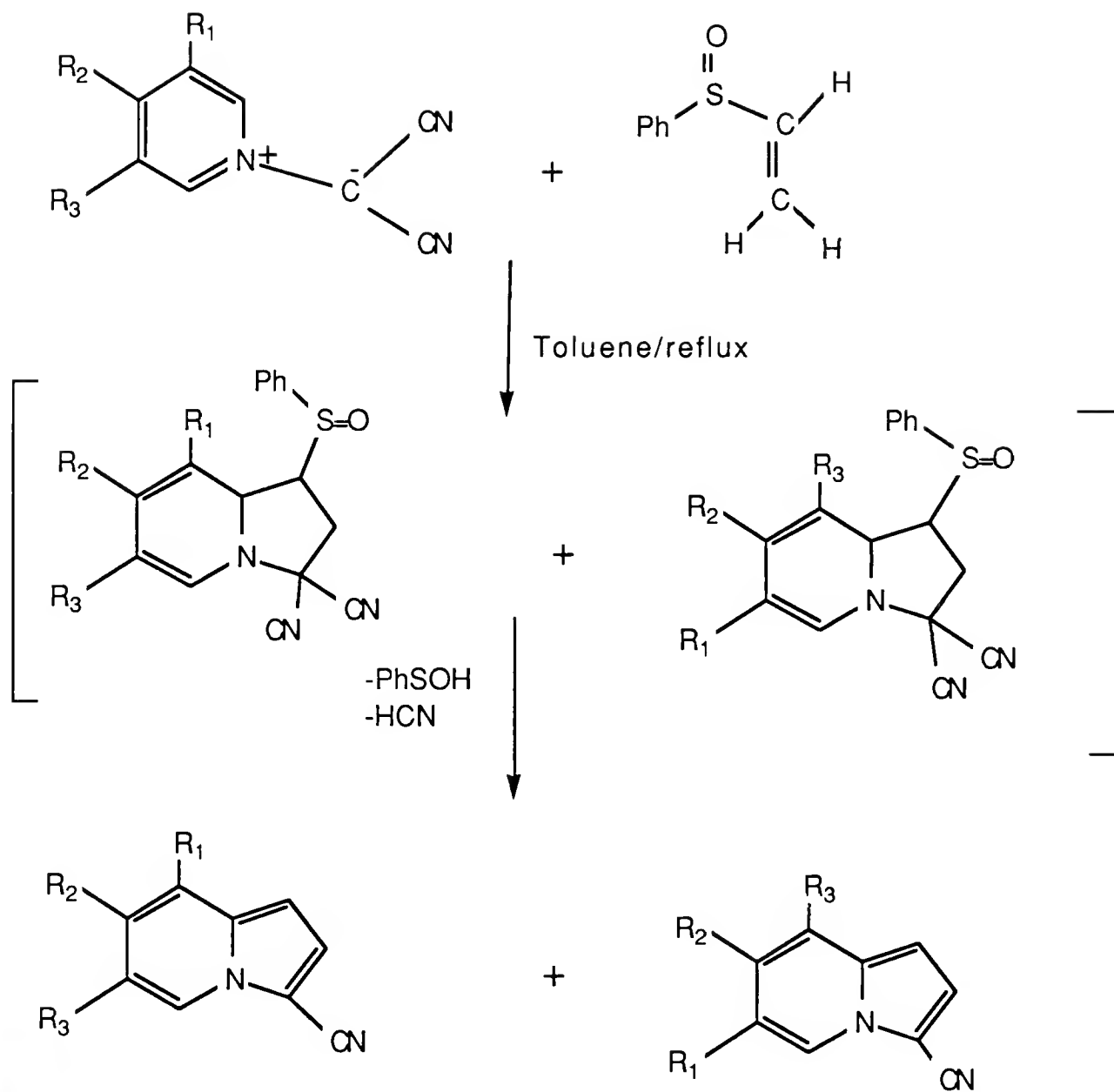


Figure 4-8. Use of PVS as an acetylene equivalent in 1,3 dipolar cycloaddition.

The polymer film after elimination became heterogenous as a result of the "spitting out" of the benzene sulfenic acid (Figure 1-1). Thus the polymer film had to be scraped out. The polymer after elimination was found to be brittle. It was insoluble in all solvents. It was characterized by IR, TGA, XPS and elemental analysis. Results of the characterization by IR, TGA, and XPS will be discussed in the appropriate sections in this chapter. Elemental analysis on the thermolyzed homopolymer showed 3.0% sulfur content (90% loss of sulfur). Elemental analysis on the thermolyzed copolymer did not show any traces of sulfur.

Some of the products of elimination condensed on the side of the tube outside the furnace in the form of crystalline needles. Much of it also condensed in the cold trap. The eliminated products obtained from the condensation in the cold trap showed a slew of products in GC and gave no useful information. However the products of elimination obtained as crystalline needles from the side of the tube showed two major peaks in the GC consisting of a lower boiling fraction (86.8%) and the higher boiling one (11.9%). From mass spectrometry, ^1H NMR and ^{13}C NMR (Figure 4-9), the lower boiling elimination product was identified as diphenyl disulfide (Ph-S-S-Ph) whereas higher boiling product was identified as benzenesulfonothioic acid, S-phenyl ester ($\text{Ph-SO}_2\text{-S-Ph}$) (phenyl benzenethiolsulfonate).

Fate of Phenyl Sulfenic Acid.

Sulfenic acids are notorious for their instability [3, 69-76]. Only in very few cases have they proved capable of actual isolation [74, 75, 76]. Shelton and Davis [74] report isolation of t-butylsulfenic acid. Penicillin

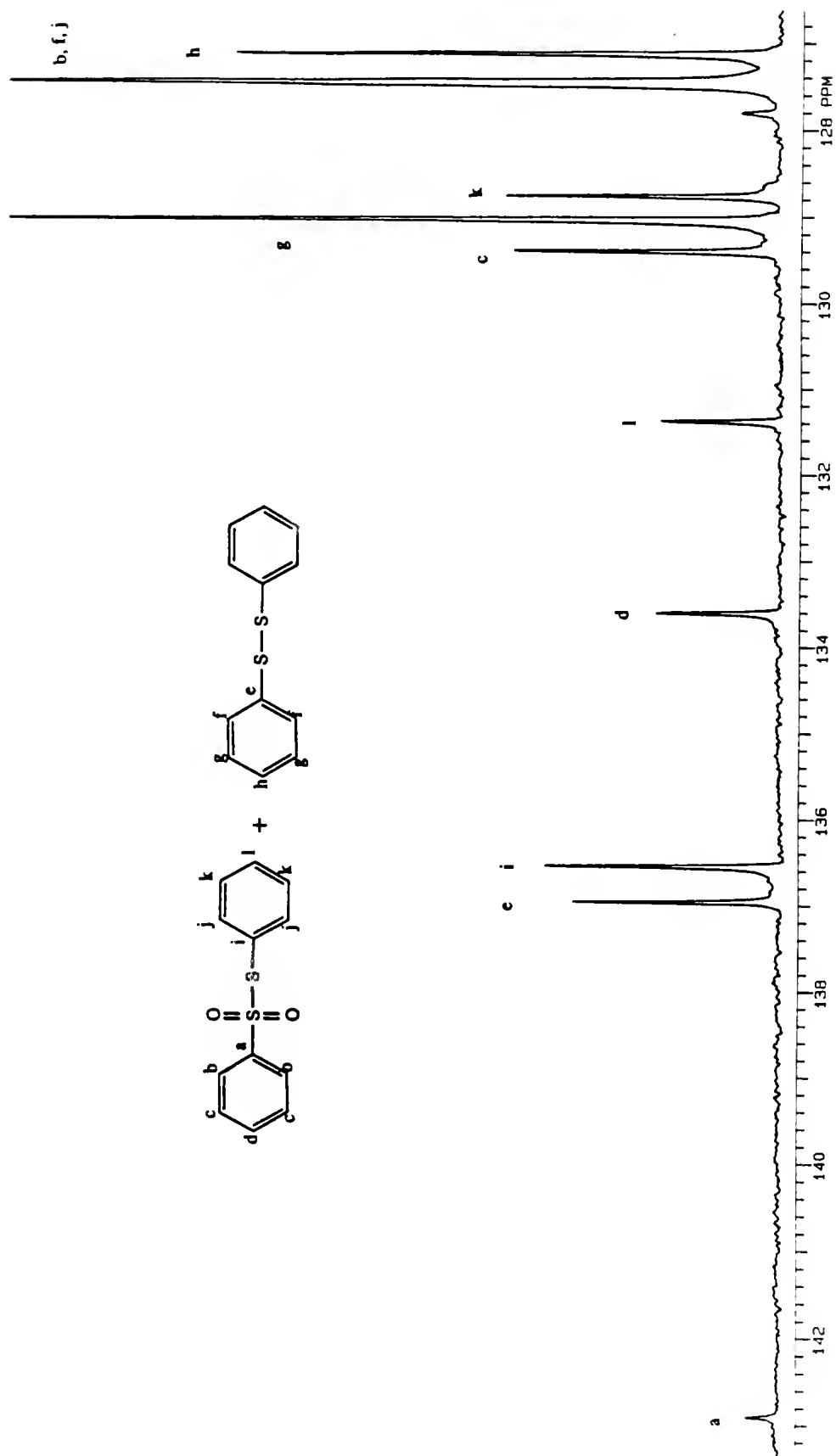


Figure 4-9. 50 MHz ^{13}C NMR of the products of elimination of phenyl sulfenic acid from PPVS.

sulfenic acid, anthraquinone sulfenic acids have been the only other sulfenic acids known [72].

Sulfenic acids under ambient conditions dehydrate immediately to form the anhydride. In our case phenyl sulfenic acid is expected to dehydrate to give the anhydride benzenesulfinothioic acid, S-phenyl ester (Ph-S(O)-S-Ph) (phenyl benzenethiolsulfinate). This dehydration reaction is shown in Figure 4-10.

The sulfenic acids associated by hydrogen bonding may be functioning as both S nucleophiles and S electrophiles [72]. The sulfenic acid dehydration reaction is essentially irreversible. Kice and Cleveland [75] suggest that the dehydration reaction in phenyl sulfenic acid is favored over its hydration (hydrolysis of the phenyl benzenethiolsulfinate) by a factor of at least 10^6 .

The thiolsulfinate itself is not thermally stable [73] and disproportionates rather readily. Fava did extensive kinetic and mechanistic studies on the disproportionation of aryl arenethiolsulfonates [73]. They found that the rate equation of disproportionation of thiosulfonates contain one first-order and one three-halves-order term. This form of rate equation suggested a unimolecular decomposition along with an induced decomposition. The first order path was due to the homolytic fission of the labile S(O)-S bond to give a sulfinyl and a thiyl radical (Figure 4-11, equation i). Dimerization of the thiyl radical gives diphenyl disulfide (Figure 4-11, equation ii). Dimerization of the sulfinyl radical give phenyl benzenesulfonothioic acid through an anhydride intermediate (Figure 4-11, equation iii). However, in this case as well as our's the ratio of disulfide to thiolsulfonate is found to be greater than one (from GC shown above) which indicates formation of other products besides

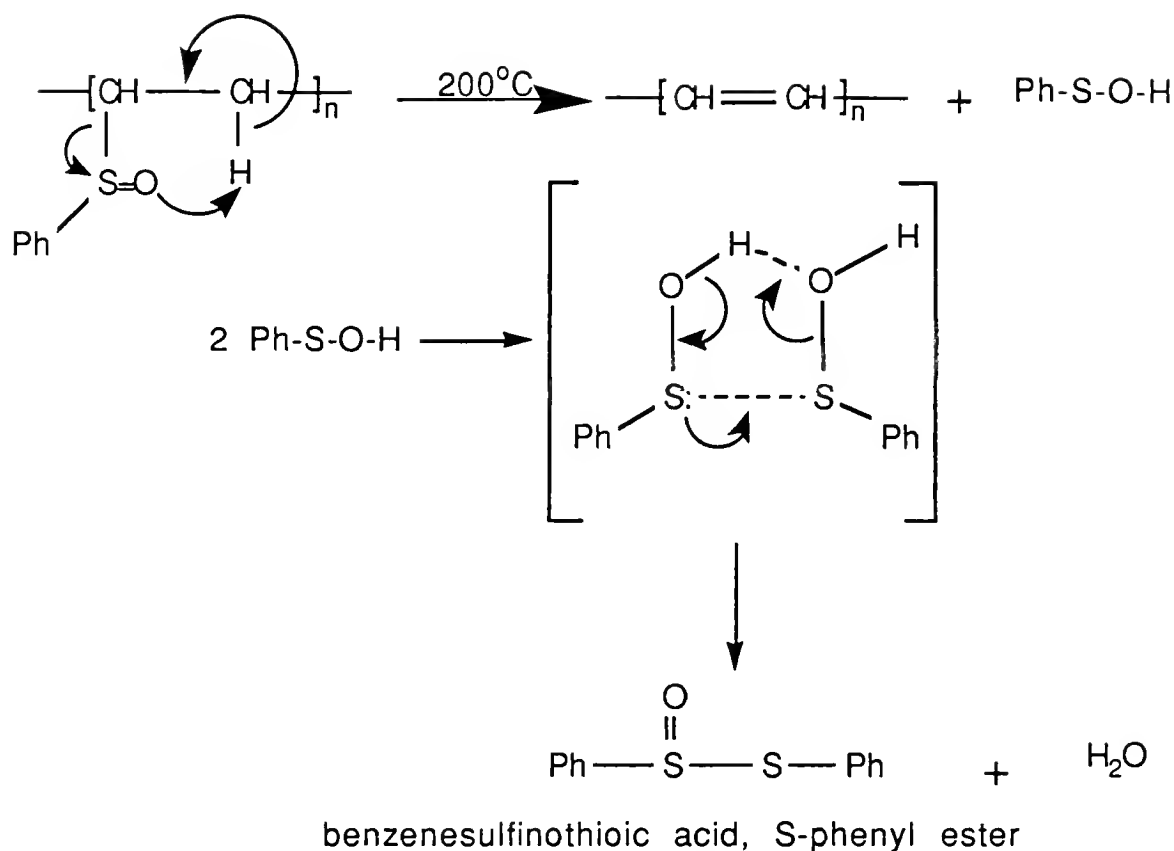


Figure 4-10. Dehydration of phenyl sulfenic acid.

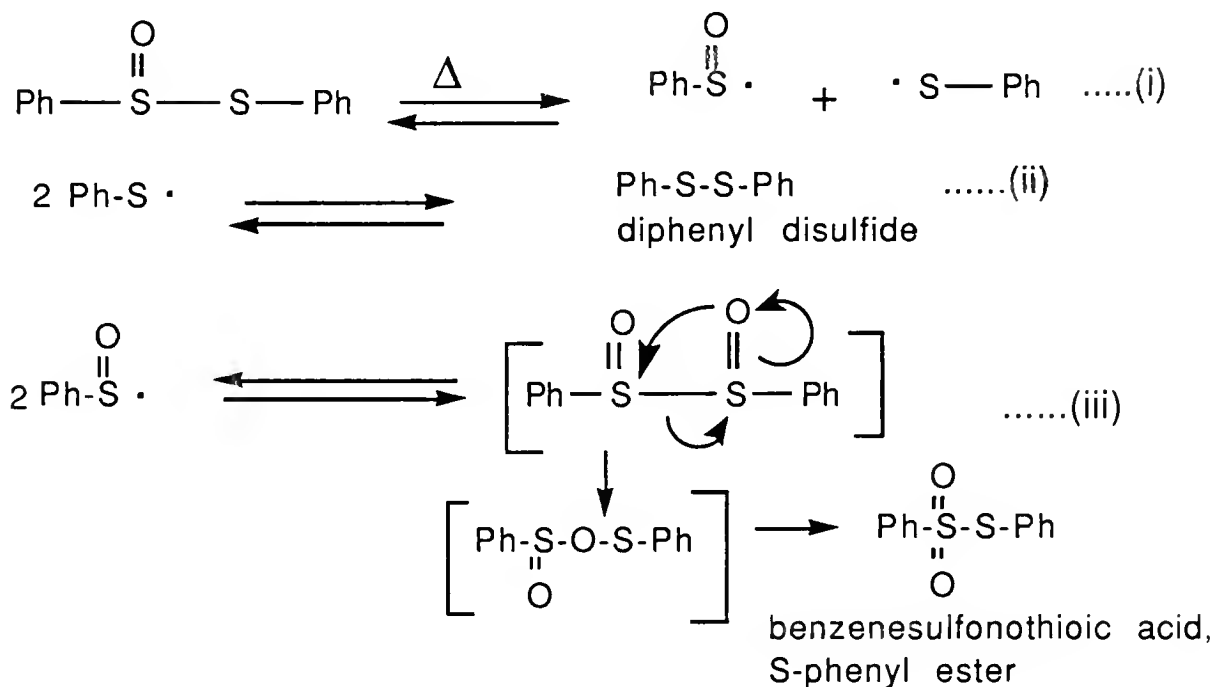


Figure 4-11. Disproportionation of benzenesulfinothioic acid, S-phenyl ester.

the two detected. Fava [73] suggested the formation of sulfonic anhydride ($\text{Ph-SO}_2\text{-O-SO}_2\text{-Ph}$) which undergoes further fragmentation and recombination. The reactions in Figure 4-11 were also consistent with the pyrolysis-MS of homo PPVS. The mass spectra of the elimination products will be discussed below.

Thermal Methods for Study of Elimination

Thermogravimetric Analysis (TGA)

TGA involves the continuous monitoring of loss in weight of a sample as it is heated at a constant rate of change of temperature or a change in weight with time at a constant temperature. The heating is usually carried out in an inert gas flow (nitrogen, 50 ml/min) (Chapter 2).

The polymer was ground into a fine powder. Usually a sample size of two mgms was used for most runs. A heating rate of $10^\circ\text{C}/\text{min}$ was employed from 50°C to 900°C .

PPVS Homopolymer

PPVS homopolymers show two distinct stages of decomposition (Table 4-1). Most thermograms also show loss of moisture/solvent etc., which may have been entrapped in the polymer matrix, at around 100°C .

The first stage of decomposition shows an onset at around 120°C and reached a maximum rate (seen from its first derivative) at around 200°C . There is usually an 80% loss in the first stage which corresponds to the elimination of phenyl sulfenic acid (Figure 4-12a). The theoretical loss of phenyl sulfenic acid would correspond to 83% loss assuming complete elimination of phenyl sulfenic acid. The temperature of elimination of phenyl sulfenic acid from PPVS homo- and copolymers is lower than most vinyl polymers containing pendant electronegative groups X which can on

Table 4-1. TGA data for (a) PPVS homopolymers. (b) After thermal elimination of phenyl sulfenic acid in vacuo at 200°C for 2 hrs. (c) After oxidation of PPVS to poly(phenylvinylsulfone). (d) Genuine polyacetylene sample.

Sample	First Stage		Second Stage
	TONSET °C ⁱ	TMAX °C ⁱⁱ	TMAX °C ⁱⁱⁱ
a. PPVS	120.2	205.2	480
	125.2	208.0	450
	134.2	210	460
(+)-PPVS	117.0	177	480
b. Thermolysed PPVS	--	--	453
c. PPVO	209	310	--
d. polyacetylene	--	--	476

- i. Temperature of onset of decomposition determined from the first derivative of the TGA curve (First Stage).
- ii. Temperature at maximum rate of decomposition determined from the first derivative of the TGA curve (First Stage).
- iii. Temperature at maximum rate of decomposition determined from the first derivative of the TGA curve (Second Stage).

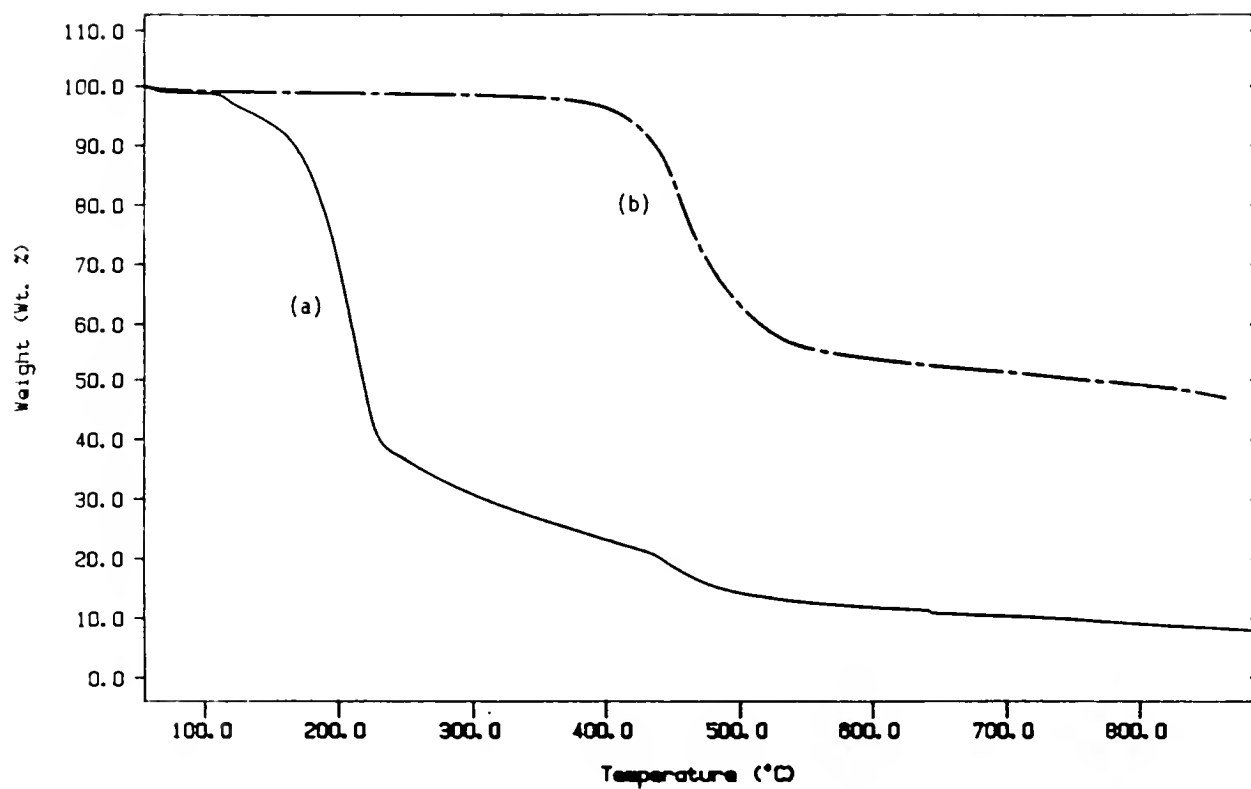


Figure 4-12. Weight % vs Temperature (TGA) curves for PPVS homopolymer: (a) Before thermolysis and (b) After thermal elimination of phenyl sulfenic acid in vacuo at 200°C for 2 hrs.

elimination of HX give polyacetylene-like polymers. This was extensively studied by Montaudo et al. [78].

The TGA thermogram of (+)-PPVS shows some unique features. There is a considerable decrease in the thermal stability of the optically active polymer as evident from a decrease in the temperature of maximum rate of elimination (175°C). Apparently stereoregularity of (+)-PPVS translates into decreased thermal stability.

The elimination of phenyl sulfenic acid would be expected to be a cyclic, sigmatropic, six-electron elimination as shown before. A "zipper" mechanism is most likely; the formation of one double bond would create a "seed" for the propagation of the next and so on down the chain. It has been well-documented in sulfoxide eliminations [63, 69] that the ease of hydrogen abstraction decreases in the order allylic > benzylic > secondary > tertiary. Thus, formation of one double bond would create an allylic site for the next and elimination would proceed more easily.

The phenyl sulfenic acid once eliminated would immediately dehydrate (see above) forming the thiolsulfinate ester which itself undergoes disproportionation to the thiolsulfonate ester and the disulfide. Thus ultimately the products of disproportionation of the thiolsulfinate ester are obtained. None of the phenyl sulfenic acid would be expected and none was seen by GC, MS, etc.

The second stage of decomposition in the TGA of the homopolymer shows a maximum rate of decomposition around 450°C . This is typically the temperature at which the polyene sequences in polyacetylene start to degrade yielding various alkyl aromatics [78, 80, 81]. A discussion of polyacetylene decomposition will follow in the section of pyrolysis-MS.

Table 4-1 also summarizes the data from the TGA curves of the thermolysed PPVS. The thermogram (Figure 4-12b, Figure 4-13a) is conspicuous by the total absence of the first step of decomposition seen in the precursor (\pm) PPVS at around 200°C. The TGA curve of the thermolysed PPVS is comparable to the thermogram of polyacetylene (Figure 4-13b, Table 4-1 entry d). The sample of polyacetylene was made in our group by Dr. K. Al-Jumah using the Shirakawa catalyst [12]. The thermogram of thermolysed PPVS is also comparable to the second step of degradation in the vinyl polymers studied by Montaudo [78] and TGA of polyacetylene from the literature [80, 81].

The thermal elimination of phenyl sulfenic acid is seen only in sulfoxides. On oxidation of PPVS to poly(phenylvinylsulfone) (PPVO) the polymer becomes thermally stable. This is corroborated by the TGA curve of PPVO (Entry c, Table 4-1). Only one degradation step is seen at a high temperature (300°C). Thus we see a distinct difference in the thermal behavior of sulfoxides and sulfones.

Styrene-PVS Copolymers

Table 4-2 summarizes the TGA data of the copolymers of styrene and PVS and Figure 4-14 shows a typical thermogram of styrene-PVS copolymer. Once again two distinct stages of decomposition are seen in the TGA thermogram of the copolymer (both A-B and A-B-A). The first stage of decomposition shows an onset which varies from 120-140°C. However the maximum rate of elimination is around 210°C for most polymers. This corresponds to the first stage in the decomposition of homo PPVS wherein phenyl sulfenic acid would be expected to eliminate through a sigmatropic elimination step to form what would be styrene-acetylene block copolymers. It is significant to note that polystyrene degrades at a

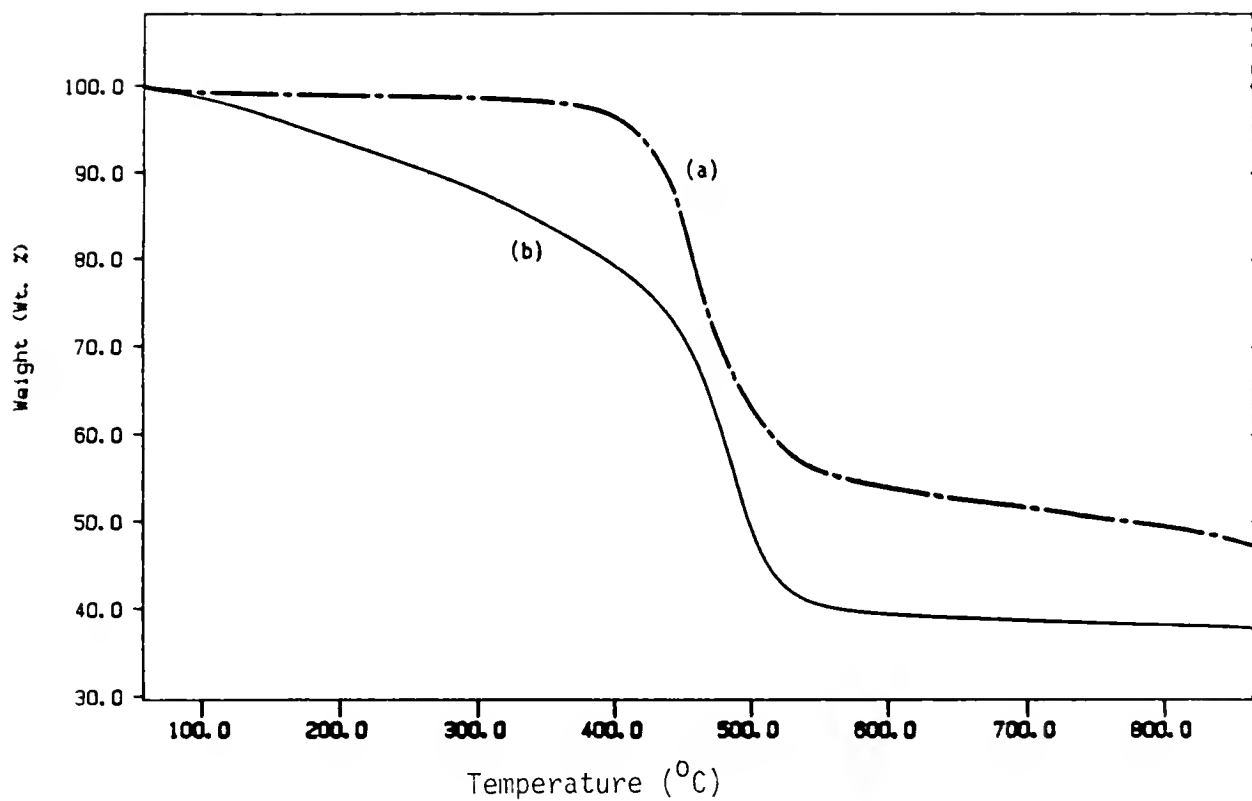


Figure 4-13. Weight % vs Temperature (TGA) curves for (a) Thermolysed PPVS homopolymer and (b) Polyacetylene.

Table 4-2. TGA data of styrene-PVS A-B diblock and A-B-A triblock copolymer.

Sample	First Stage		Second Stage
	TONSET °C ^a	TMAX °C ^b	TMAX °C ^c
1 polystyrene	--	--	445
2 AB21 ^d	120	205	422
3 AB53	138	208	446
4 AB66	139	222	447
5a AB85	127	216	437
b HAB85 ^e	--	--	460
c OAB85 ^f	200	310	--
6 AB90	137	217	432
7a ABd8	120	196.5	417
b HABd8 ^g	--	--	448
8 ABA30 ^h	130	205	445
9 ABA50	148	215	424
10 ABA78	150	211	454
11 ABA90	140	207	436
12a ABAd8	144	212	457
b HABAd8 ⁱ	--	--	450
13 ABAS0	142	210	450
14a ABAS1	136	207	441
b HABAS1 ^j	--	--	425

- a. Temperature of onset of decomposition determined from the first derivative of the TGA curve (First Stage).
- b. Temperature at maximum rate of decomposition determined from the first derivative of the TGA curve (First Stage).
- c. Temperature at maximum rate of decomposition determined from the first derivative of the TGA curve (Second Stage).
- d. For information on the A-B copolymers see Table 3-4.
- e. Thermolysed AB85.
- f. Oxidised AB85.
- g. Thermolysed ABd8.
- h. For information on the A-B-A copolymers see Table 3-5.
- i. Thermolysed ABAd8.
- j. Thermolysed ABAS1.

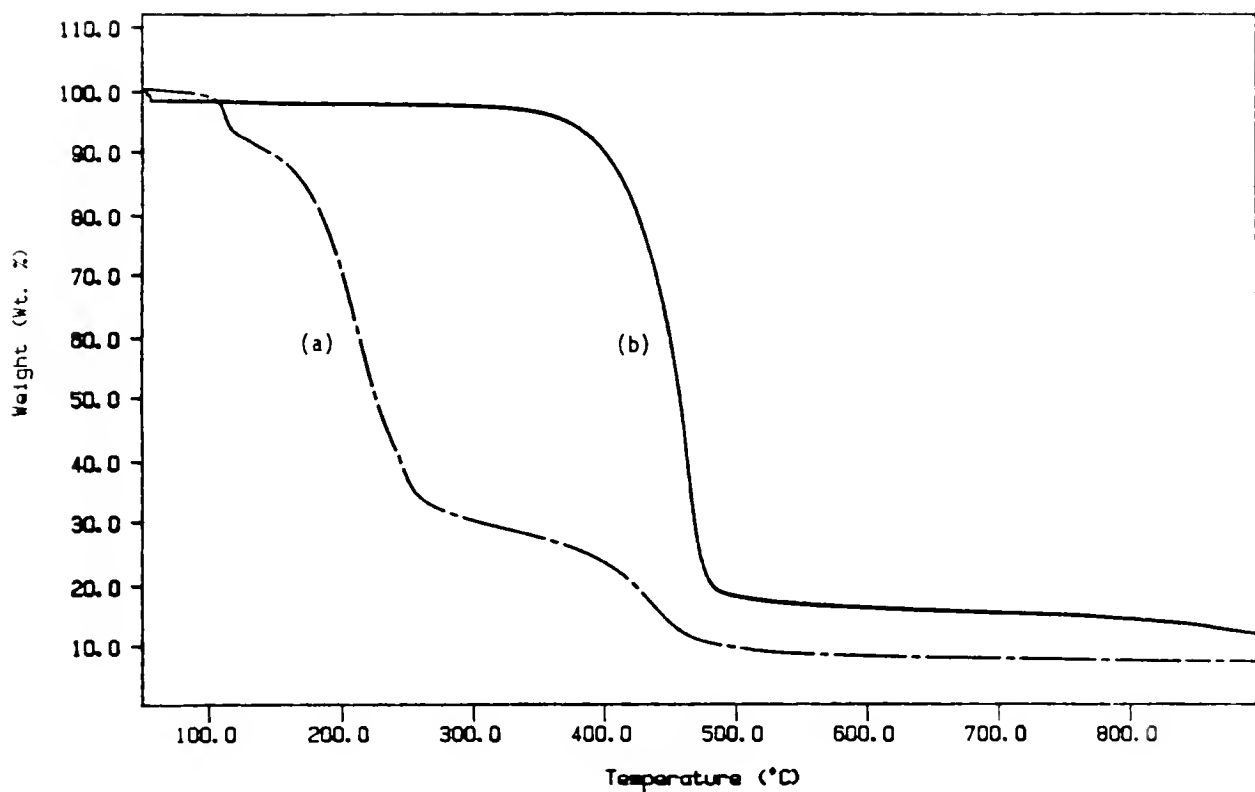


Figure 4-14. Weight % vs Temperature (TGA) curves for Styrene-PVS copolymer (sample AB-85, Table 4-2) (a) Before thermolysis and (b) After thermolysis in vacuo at 190°C for 1.5 hrs.

much higher temperature (Entry 1, Table 4-2). Thus at the lower temperatures used for the elimination of phenyl sulfenic acid the polystyrene block would be mostly unaffected. This is also shown by pyrolysis-MS which will be discussed later.

The second stage of decomposition in the block copolymers occurs around 440-450°C which is the temperature at which styrene depolymerizes by an unzipping mechanism (Entry 1, Table 4-2) [82, 83] and at which the polyene sequences of the polyacetylene block rearrange and decompose to yield various aromatic hydrocarbons [80, 81].

The sample AB85 containing 74.9% of sulfoxide in the A-B copolymer was oxidized as before using 30% H₂O₂. The oxidized copolymer, interestingly enough, shows only one high temperature degradation stage (Entry 5C, Table 4-2), although one would expect to see two stages corresponding to the sulfone decomposition at 300°C and polystyrene depolymerization at 450°C.

Several copolymers were subjected to thermolysis in vacuo at 190°C. The products are brittle cellophane like transparent yellow films. The TGA of the heated copolymers is also summarized in Table 4-2 (Entries 5c, 7b, 12b, and 14b). Once again only one high temperature degradation step was noted around 450°C. This also confirms the almost quantitative elimination of phenyl sulfenic acid from the copolymer.

Pyrolysis-Mass Spectrometry

Mass spectrometry (MS) is much less used for structure determination in polymers than in low MW organic compounds. Since MS techniques require transfer of the sample in the gas phase, the low volatility of polymers has constituted a serious drawback for the application of mass spectrometric analysis to polymer systems.

Remarkable progress was achieved when polymers were introduced directly into the mass spectrometer and pyrolysis performed close to the ion source [84]. Recent advances [84-86] in laser technology, however, have spawned a lot of interest in MS of polymer systems especially laser desorption/FT-MS [85].

Montaudou [78, 79] carried out studies of thermal degradative mechanisms in vinyl polymers with a pendant electronegative group which on elimination would lead to the formation of polyene structures. Ours being a similar system, it was decided to carry out pyrolysis-MS on PPVS homo and copolymers.

PPVS Homopolymers

Distinct differences were found in the MS of PPVS at low and high pyrolysis temperatures. The MS at low pyrolysis temperature ($<190^{\circ}\text{C}$) is consistent with the elimination of phenyl sulfenic acid and its further reactions. The positive ion fragments (m/z) in the pyrolysis-MS of homo PPVS at 190°C along with the assignments of the peaks are summarized in Table 4-3. The m/z 218 (Ph-S-S-Ph) absorption was observed as the base peak. The MS was compared with the actual MS reported in the EPA/NIH Mass Spectral Data Base. From the comparison we conclude that the MS observed at low temperatures is mainly due to Ph-SO-S-Ph, Ph-SO₂-S-Ph and Ph-S-S-Ph that were also previously identified.

There was no indication of presence of phenyl sulfenic acid which corroborates our conclusion that it dehydrates to the sulfinothioic ester immediately upon formation (Figure 4-10). Although the presence of Ph-SO-S-Ph is detectable it is mainly its disproportionation products (Ph-SO₂-S-Ph and Ph-S-S-Ph) (Figure 4-11) that constitute the MS at low temperatures.

Table 4-3. Data from the pyrolysis-M.S. of homo PPVS at 190°C.

Positive Ion Fragments	M/Z
Ph-S-S-Ph	218 Base peak
Ph-SO ₂ -S-Ph	250
Ph-S-Ph	185
Ph-Ph	154
Ph-SO ₂	141
Ph-SO	125
Ph-SH	110
Ph-H	78
H ₂ O	18

Table 4-4. Data from the pyrolysis-M.S. of homo PPVS at 450°C.

Positive Ion Fragments	M/Z
Ph-SH	110 Base peak
propyl anthracene	220
ethyl anthracene	206
methyl anthracene	192
anthracene	178
propyl naphthalene	170
ethyl naphthalene	156
methyl naphthalene	142
naphthalene	128
propyl benzene	120
xylene	106
toluene	91
benzene	78
H ₂ O	18

At high pyrolysis temperatures ($>400^{\circ}\text{C}$) a totally different picture emerges (Table 4-4). The base peak is m/z 110 (PhSH) which indicates presence of the decomposition products in the polymer matrix (mainly PhSSPh and PhSO_2SPh). However the most intense peaks are due to alkyl-aromatic hydrocarbons, seen as periodic clumps of high mass peaks [78, 79]. Polyacetylene exhibits a similar pyrolysis-MS at 490°C [78] showing toluene as the base peak and other substituted aromatics of higher masses.

According to Chien et al. [81] in the pyrolysis of polyacetylene the initiation process of degradation is probably the thermal excitation of bonding π electrons to the antibonding state resulting in bond dissociation to form vinyl radicals (Figure 4-15) followed by intramolecular electron migration and ring closure leading directly to benzene. Other alkyl-aromatics can be accounted for by a series of proton-electron migrations which may be quantum-mechanical tunneling in nature. The formation of alkyl-aromatics probably involve cleavage of cross-linked polyacetylene chains at high temperatures ($>450^{\circ}\text{C}$) (Figure 4-15) [78].

Styrene PVS Copolymers

Like the homopolymer, the copolymer also shows distinct differences in the decomposition at low and high pyrolysis temperatures.

At low temperatures ($<190^{\circ}\text{C}$) (Table 4-5) once again we see the MS due to the elimination of phenyl sulfenic acid and its further reactions. From the total ion current it is seen that the polystyrene block is mostly unaffected even at 225°C . Formation of styrene, which is indicative of depolymerization of the polystyrene block, is only beginning around 225°C . This result was significant for our purpose since we can safely carry out

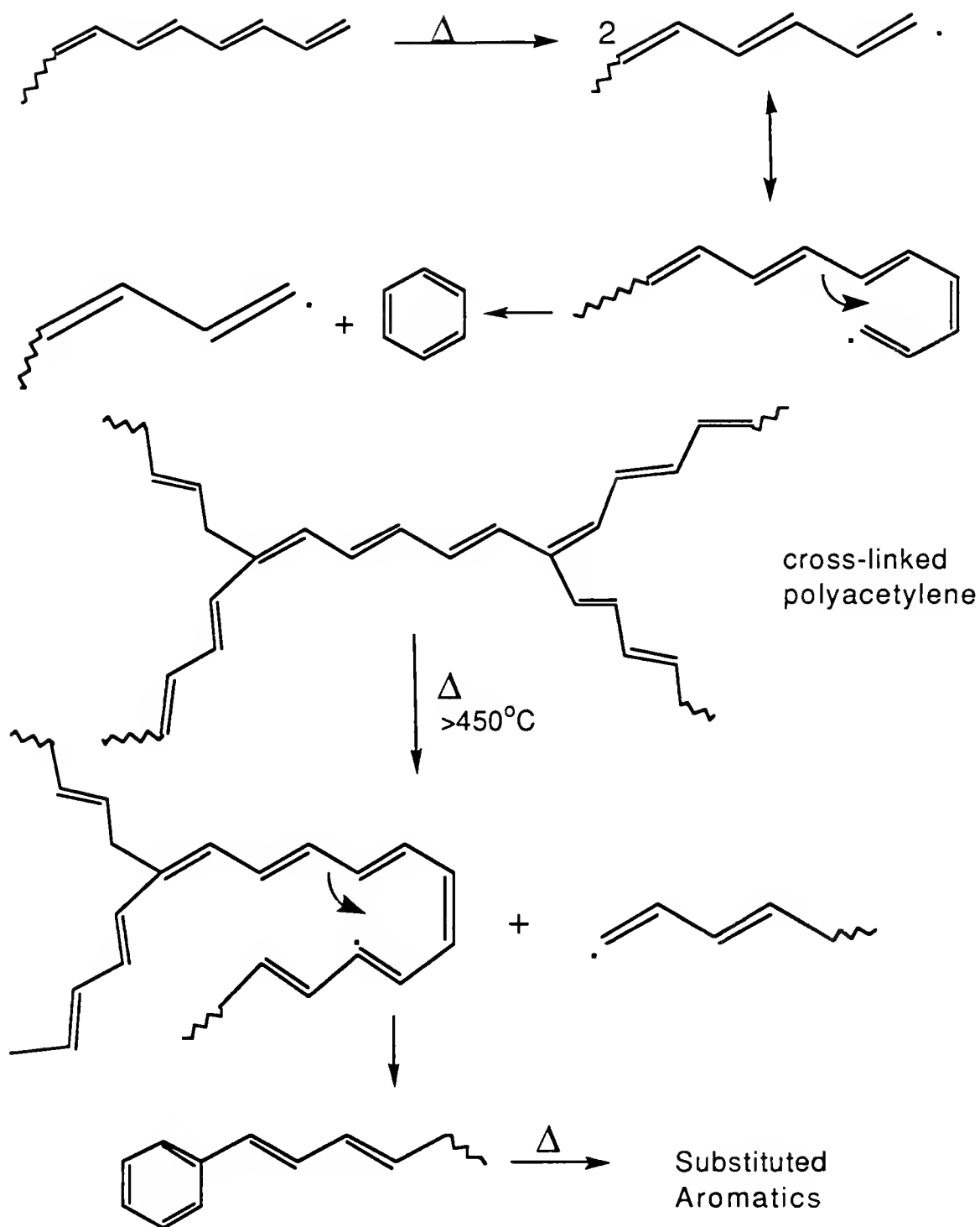


Figure 4-15. Scheme for the formation of alkyl-aromatics in the pyrolysis of polyacetylene at high temperatures ($>450^\circ\text{C}$).

Table 4-5. Data from the pyrolysis-M.S. of styrene-PVS copolymer at 150°C.

Positive Ion Fragments	M/Z
Ph-S	109 Base peak
Ph-SO ₂ -S-Ph	250
Ph-S-S-Ph	218
Ph-S-Ph	185
Ph-Ph	154
Ph-SO ₂	141
Ph-SO	125
Ph-SH	110
Ph-H	78
Ph	77
H ₂ O	18

Table 4-6 Data from the pyrolysis-M.S. of styrene-PVS copolymer at 435°C.

Positive Ion Fragments	M/Z
Ph-CH=CH ₂	104 Base peak
propyl anthracene	220
ethyl anthracene	206
methyl anthracene	192
anthracene	178
naphthalene	128
propyl benzene	120
toluene	91
benzene	78

the elimination of the copolymers at lower temperatures without significantly degrading the polystyrene block in the copolymer.

Formation of styrene is greatly accelerated at temperatures above 250°C and in fact above 300°C styrene becomes the base peak in the MS (Table 4-6). Once again at higher temperatures we see (although to a lesser extent because of polystyrene degradation) alkyl-aromatics typical of polyacetylene decomposition.

Studies of the Elimination of PPVS by Spectroscopic Methods X-Ray Photoelectron Spectroscopy (XPS)

XPS or electron spectroscopy for chemical analysis (ESCA) is generally regarded as a key technique for surface characterization and analysis of polymers. This technique provides a total elemental analysis of the top 10-100 Å of any solid surface or film [87, 88].

The basic principle of XPS is the photoelectric effect. Low energy X-rays (magnesium K- α) impinge the surface of a thin film. Absorption of these X-rays results in interaction with one of the core atomic orbital electrons such that there is a total and complete transfer of the energy of the photon to the electron. Since the photon energy is greater than the binding energy of the electron in the atomic orbital, the electron is ejected from the atom. The total energy of the X-ray photon must be accounted for and to a first approximation it is partitioned in two ways. One of the components is the binding energy of the electron E_b and can also be thought of as the energy required to remove the electron from the atom or the ionization energy of the electron. The energy in excess of E_b appears as the kinetic energy of the electron after it is emitted (E_k). It is this kinetic energy that the spectrometer measures and hence calculates the binding energy of the electron. Thus the basic equation for XPS is

$$E_b = h\nu - E_k$$

where $h\nu$ is the energy of the X-ray photon.

The X-ray photons statistically interact with the atomic and molecular orbital electrons in the sample. Some fraction of the photoelectrons produced are directed up and out of the sample and analyzed by the analyzer which basically measures the number of electrons and their different kinetic energies and produces a spectrum of photoelectron intensity as a function of binding energy. The binding energy (B.E.) position of each of the key peaks allows identification of the atoms involved and measuring the area under each peak allows quantitation of each of the elements present on the surface of the polymer film. There are many variables involved and there may be charging effects of the sample which would tend to shift the B.E. from sample to sample. Thus an internal reference has to be used for calibration. Commonly this is the carbon 1s peak at 285.0 eV.

We used XPS for a) surface elemental composition of PPVS homo- and copolymers, b) surface elemental composition for the homo- and copolymers after thermolysis, c) determination of the oxidation of sulfoxides to sulfones, and d) to monitor changes on the surface of the polymers upon heating in the XPS spectrometer.

Table 4-7 summarizes the data obtained on various samples. The B.E.s are reported with respect to the C1s peak (285 eV). In the homo-PPVS (entry 1, Table 4-7) the sulfoxide sulfur shows a S2p B.E. of 166 eV. This is comparable to the sulfoxide S2p B.E. of 165.9 eV in Ph₂SO reported in the literature [89]. Oxidation of PPVS to PPVO results in a shift of +3 eV (B.E. = 168.9 eV for PPVO, Entry 2, Table 4-7). Oxidation of sulfoxide to

Table 4-7. Data from the ESCA spectra of PPVS homopolymers, styrene-PVS copolymers and their thermolysed and oxidized products.

Sample	Element	Binding Energy (eV)	Atomic Conc. (%), Exp'tal	Atomic Conc. (%), Calc'd
1. PPVS homopolymer	C1s	285.0	78.9	80.0
	O1s	531.3	12.2	10.0
	S2p	166.2	8.9	10.0
2. Oxidised PPVS	C1s	285.0	83.4	72.7
	O1s	532.4	11.6	18.2
	S2p	168.9	5.0	9.1
3. Thermolysed PPVS	C1s	285.0	--	--
	O1s	532.9	--	--
4. AB85 ^a	C1s	285.0	82.4	91.4
	O1s	531.6	14.9	4.3
	S2p	166.2	2.6	4.3
5. Oxidised AB85	C1s	285.0	82.2	87.4
	O1s	532.2	15.4	8.4
	S2p	169.0	2.42	4.2
6. Thermolysed AB85	C1s	285.0	91.3	100
	O1s	532.5	8.5	0.0
7. ABAS1 ^b	C1s	285.0	90.0	95.7
	O1s	532.4	8.5	2.1
	S2p	166.8	1.47	2.1
8. Oxidised ABAS1	C1s	285.0	77.0	95.0
	O1s	531.8	19.2	3.3
	S2p	168.5	3.8	1.7
9. Thermolysed	C1s	285.0	92.0	100
	O1s	534.1	7.88	0.0

a. For information on AB85 see Table 3-4.

b. For information on ABAS1 see Table 3-5.

sulfone results in a more electropositive sulfur and hence greater B.E. of the core electrons (chemical shift effect) [87].

The thermolysed PPVS does not show any presence of sulfur in the XPS spectrum. However surface oxidation, presumably during handling, resulted in an O1s peak at 533 eV (Entry 3, Table 4-7). It was seen that most of the spectra in XPS showed a decided sensitivity to surface oxidation as revealed from the inflated atomic concentration of O1s. Oxygen was also detected from the residual silicon grease in the polymer (or in the sample holder) which has a low surface free energy and tends to "creep up" during scanning. However oxygen from grease could be easily detected by a consequent absorption of the Si2s peak at 153 eV and Si2p peak at 102 eV.

There was a good correlation between the experimental and calculated atomic concentrations for PPVS. However the correlation between the experimental and calculated atomic concentration in the copolymers (both A-B and A-B-A) was seen to be quite poor. The surface free energy of a polymer is inversely proportional to the contact angle of an air bubble in water in contact with the polymer film. The contact angle of PPVS, AB and ABA copolymers and polystyrene was measured by the captive air bubble method [90] (described in the Experimental section). The contact angle varied from 50° for PPVS to 86° for polystyrene. The copolymers show an intermediate contact angle depending on the composition. From this rough experiment it was seen that PPVS has a higher surface free energy compared to the copolymers. It is thus possible that the polystyrene block in the copolymer would occupy much of the top 50-100 Å which is the range of the XPS experiment. This might be a reason

for the poor correlation between the experimental and calculated atomic concentrations in copolymers.

The oxidized copolymer AB85 (Entry 5, Table 4-7) also reveals the chemical shift effect of oxidation of sulfoxide to sulfone. The thermolysed copolymers once again do not show any presence of S2p but do show presence of O1s.

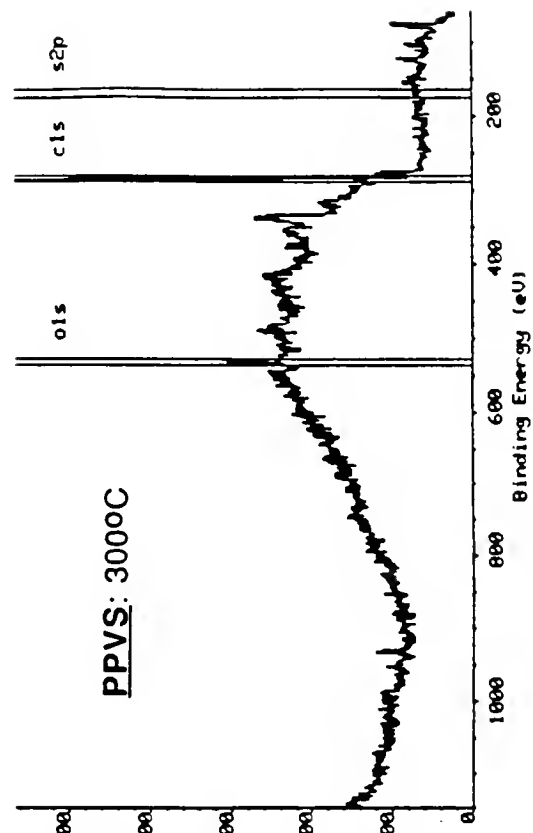
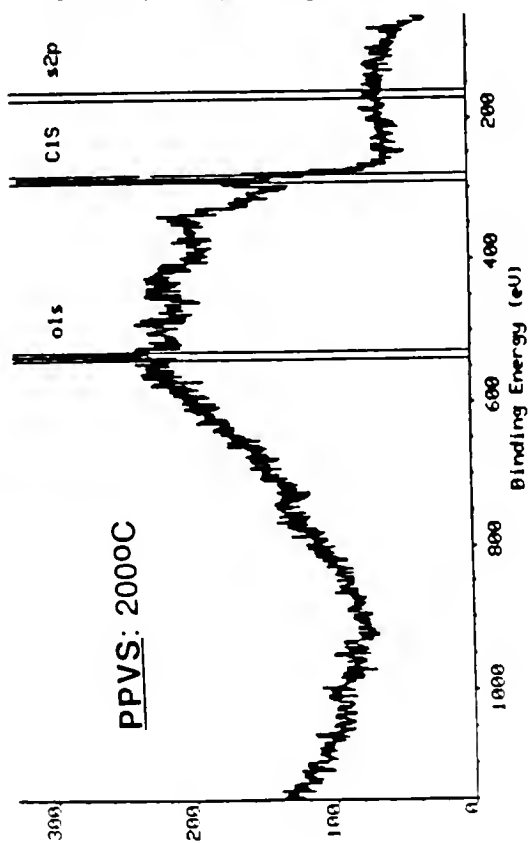
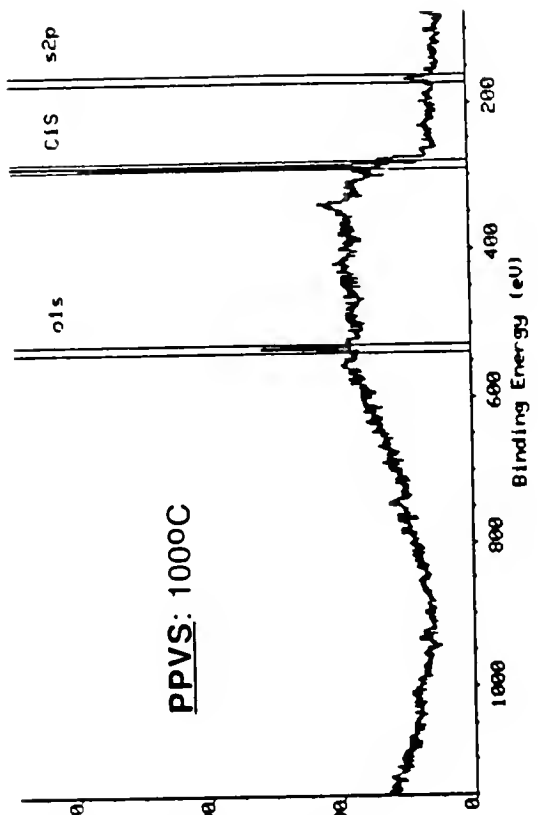
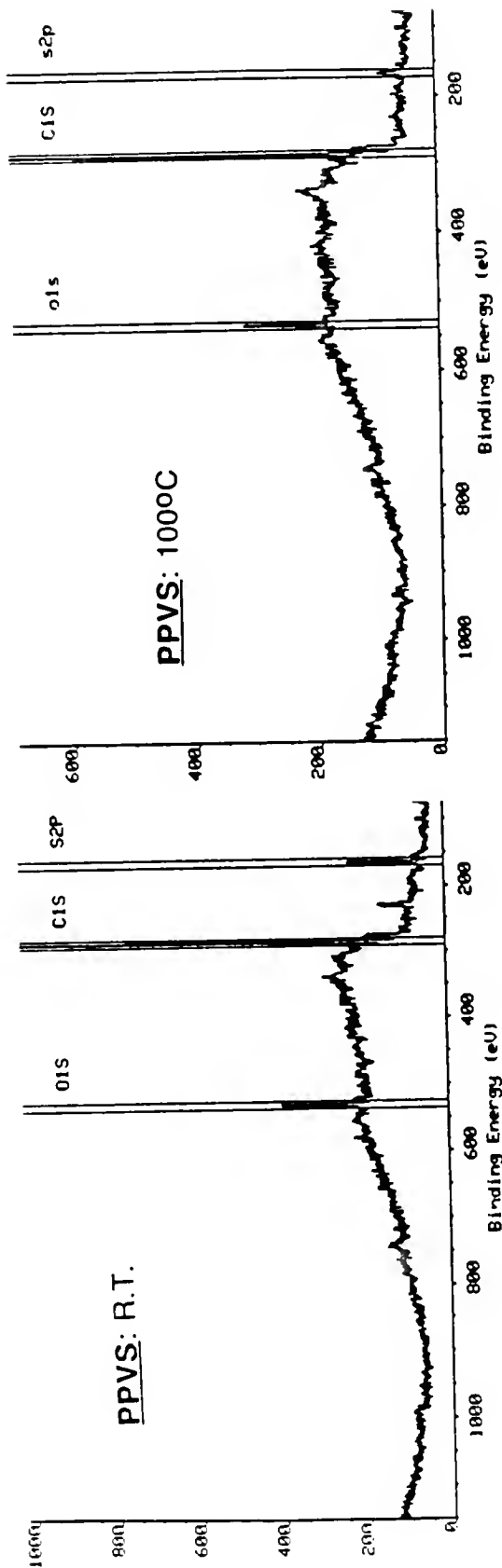
XPS was also employed to monitor the change in the polymer composition with temperature. The experimental details of high temperature XPS studies have been discussed in the Experimental section. Figure 4-16 shows the dramatic change in XPS in going from room temperature to 300°C. The S2p peak starts disappearing around 100°C. Interestingly enough although at higher temperatures (>200°C) the 166 eV S2p peak of sulfoxide completely disappears three other S2p peaks show up albeit of less intensity (Figure 4-17) at (i) 164.0 eV which could be assigned to Ph-S-S-Ph [89] and (ii) 169.0 eV and (iii) 169.5 eV which could be assigned to Ph-S(O)₂-S-Ph [89]. These are the final products of elimination. Thus we see that some of the eliminated products contaminates the polyacetylene formed. This was also seen in IR spectroscopy which will be discussed later.

Figure 4-16 also reveals the persistence of the O1s peak even at 300°C. As seen before this might be due to presence of residual silicon grease in the polymer.

Nuclear Magnetic Resonance (NMR)

One of the drawbacks of polyacetylene is its intractable nature. It is insoluble in all solvents. Spectroscopic methods involving the study of polyacetylene of necessity are thus solid-state based [1.1-1.4]. It was therefore highly desirable to see if solution properties of polyacetylene

Figure 4-16. Change in the XPS spectra of PPVS homopolymer with temperature going from room temperature to 300°C.



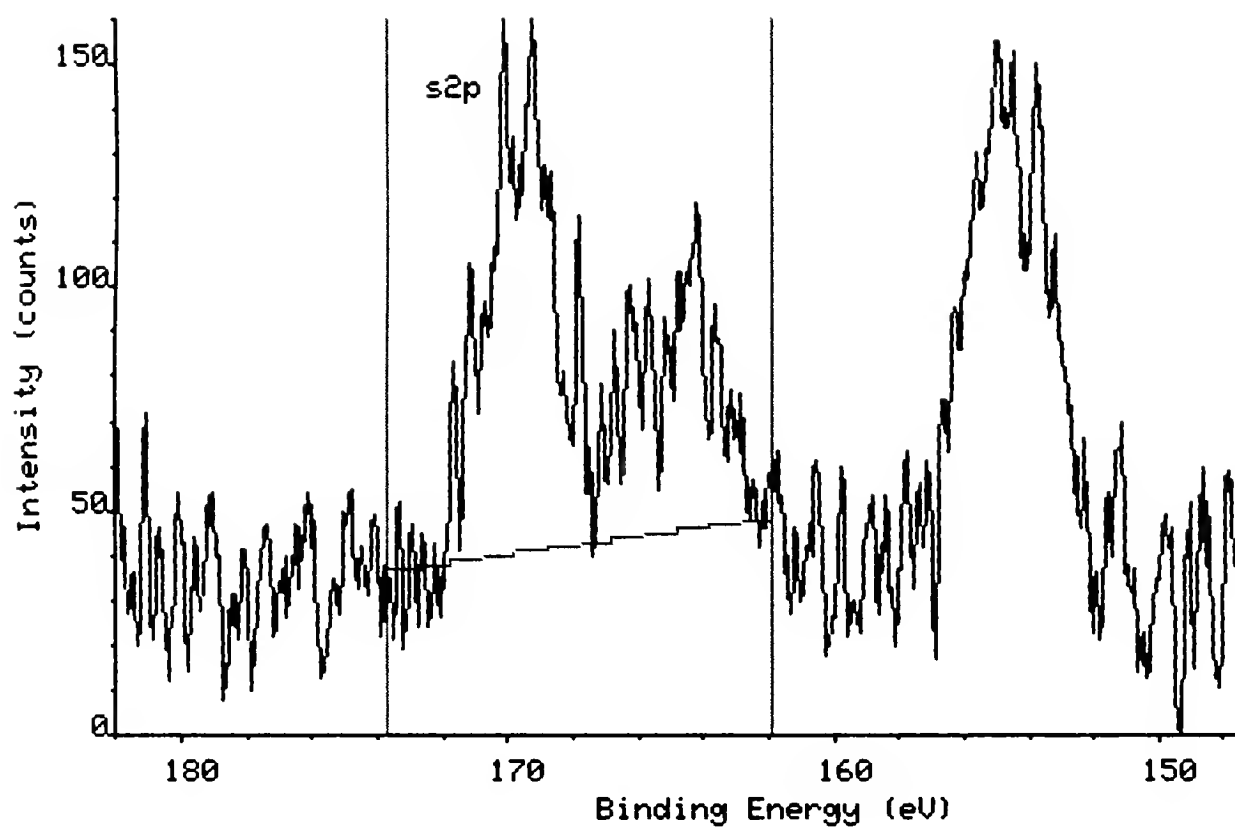
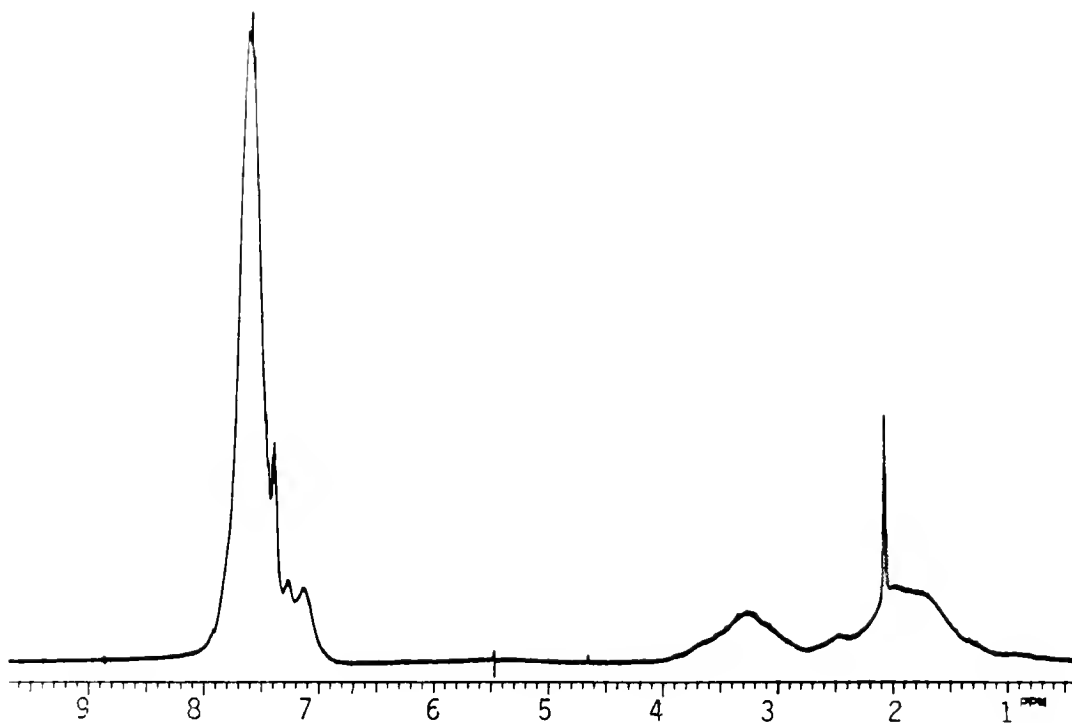


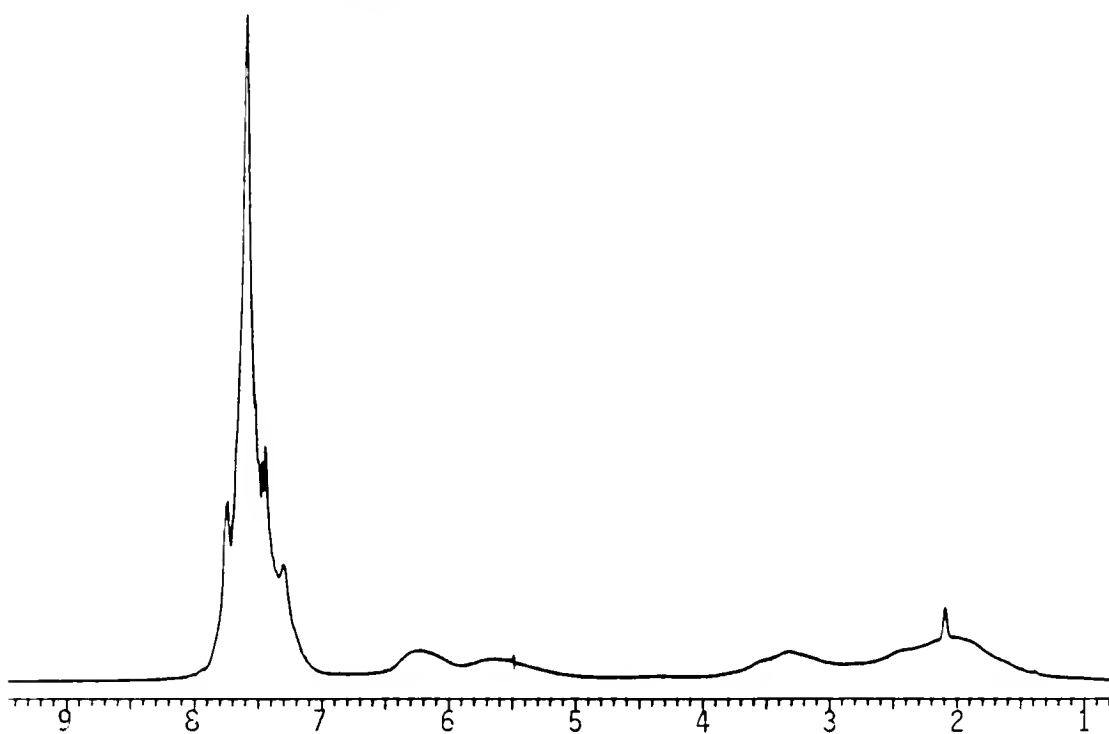
Figure 4-17. XPS spectrum of the S2p region of PPVS at 200°C.

could be measured as a block copolymer containing a soluble block. Thus our system of A-B and A-B-A copolymers of polystyrene-*b*-acetylene was a potentially attractive way to study soluble polyacetylenes. However we found that the presence of more than 10 polyene units or more than 5 mole% of polyacetylene in the copolymer renders the precursor insoluble upon thermal elimination. The copolymer AB21 (Table 3-4) containing 21-32% of sulfoxide was found to be soluble in chloroform upon elimination. It is seen that the polyene sequences in the thermolysed copolymer are overlapped by the ortho aromatic absorptions of the polystyrene phenyl (δ = 6.2-6.8 PPM). This is also confirmed by the decrease in the integration of the sulfoxide methine absorption at 3.0 PPM and sulfoxide methylene absorption at 1.8 PPM (which overlaps in the precursor sample with the methine absorption of polystyrene). It was thus decided to see if the acetylenic =CH absorption could be observed in a copolymer which is not complicated by the ortho aromatic absorptions of the polystyrene block. Thus copolymers (both A-B and A-B-A) were synthesized with styrene-*d*8. However we were unsuccessful in solubilizing the thermolysed copolymer with a high enough polyene content for NMR analysis.

The thermal elimination of phenyl sulfenic acid from PPVS was monitored by ^1H NMR from 30°C to 150°C. The polymer was dissolved in glacial acetic acid-*d*4 and sealed under a partial pressure of argon. The partial pressure of argon was necessary to improve resolution at high temperatures (private communication from Dr. Roy King). Figure 4-18 a-d dramatizes the effect of temperature on the ^1H NMR of PPVS. Several interesting features are worth noting. It is seen that up to about 100°C there was little change in the ^1H NMR. At 100°C, however, we see several

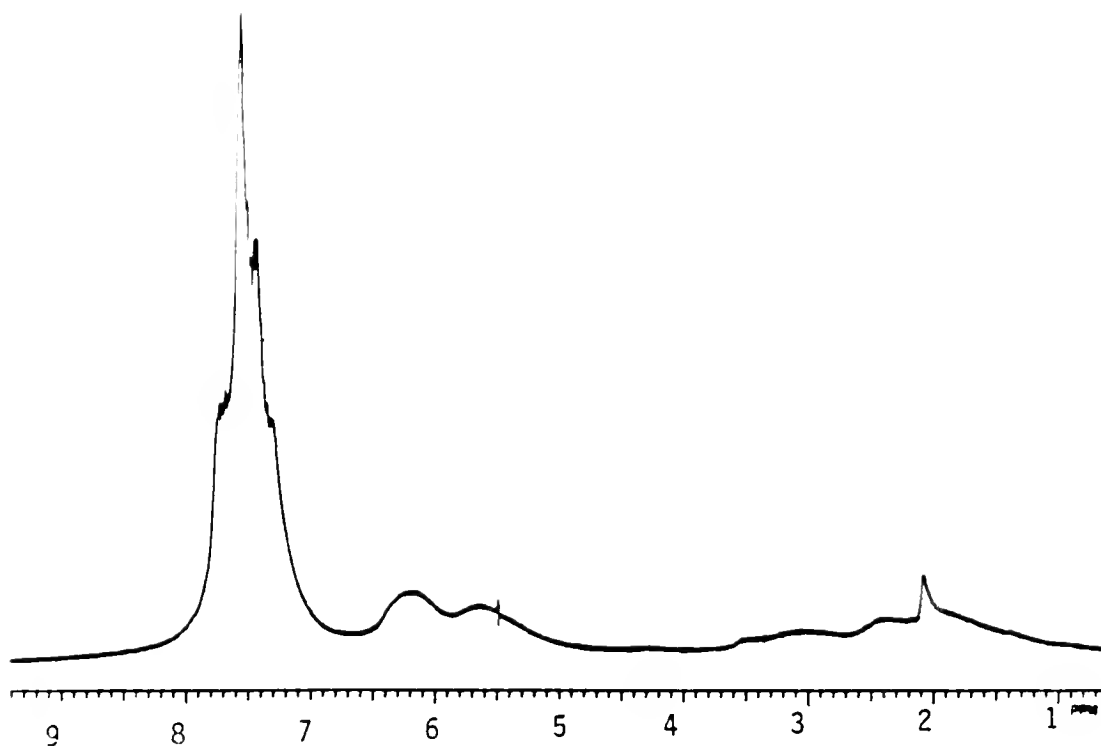


(a). Room temperature

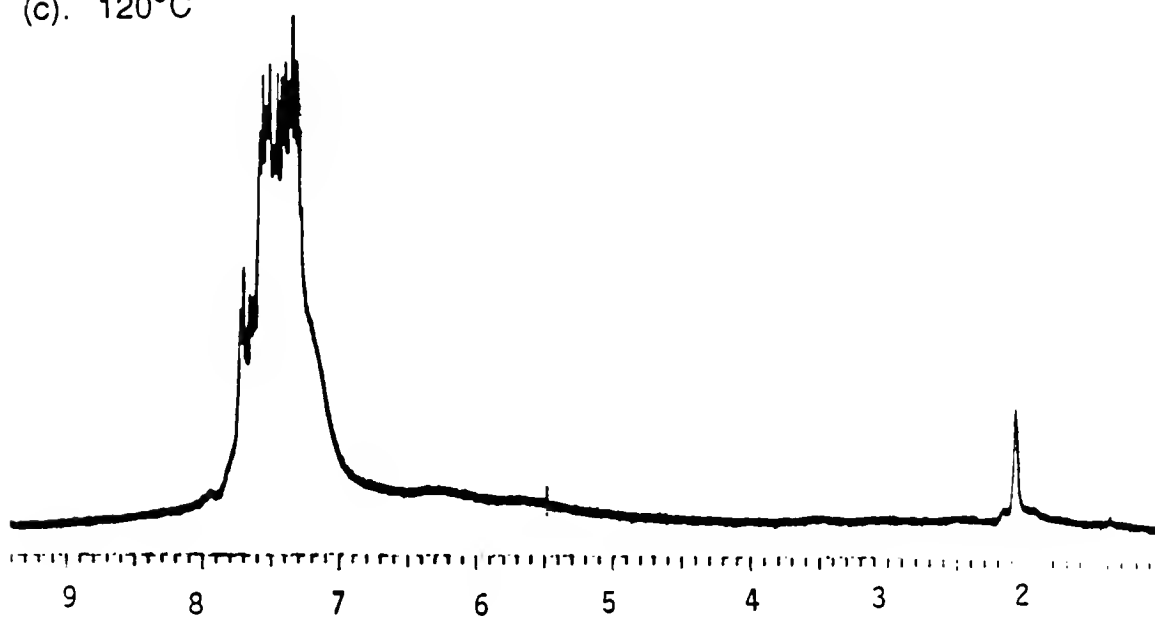


(b). 100°C

Figure 4-18. Change in the 300 MHz ¹H NMR spectra of PPVS homopolymer with temperature: (a) room temperature (b) 100°C in CD₃COOD.



(c). 120°C



(d). 150°C

Figure 4-18 (continued). Change in the 300 MHz ^1H NMR spectra of PPVS homopolymer with temperature: (c) 120°C (d) 150°C in CD_3COOD .

changes. The CH and CH₂ absorptions at δ 3.2 PPM and δ 1.8 PPM respectively show a decrease in intensity. Simultaneously we see two peaks showing up in the vinyl region at δ 5.7 and δ 6.3 PPM. The aromatic absorptions become sharper. At 120°C the above events become more enhanced. The CH and CH₂ absorptions have decreased further whereas the vinylic absorptions have intensified. At 150°C all of the peaks disappear except for the aromatic absorptions probably as a result of polymer precipitation.

We give the following interpretation of the above events. As the temperature is increased from room temperature to 100°C we see the formation of polyene linkages due to the sigmatropic 6- π elimination of phenyl sulfenic acid from PPVS as illustrated in Figure 4-19. A decrease in the -CH₂- and -CH- absorptions of the sulfoxides was noticed concurrent with the development of broad absorptions in the vinyl region. Table 4-8 summarizes the normalized area of the vinyl protons as compared to the normalized area of the sulfoxide methine from which the percentage of the polyene groups (both cis and trans) could be calculated. We see a dramatic increase in the % polyene from 80°C to 100°C (10% to 40%). Obviously the polyenes form at the expense of the methylene and methine of PPVS. The polymer is still soluble because of the presence of a substantial percentage of sulfoxide groups in the polymer (Table 4-8). Thus random and/or block copolymers may be formed. The two peaks in the vinyl region indicate two different types of olefins; cis/trans or internal/terminal. The fact that we do not see a change in the chemical shift of the polyene peaks with temperature indicate that they are most likely due to geometric isomers. Also the chemical shifts observed (δ 5.8 PPM and δ 6.3 PPM) are close to those observed in low MW conjugated cis and trans polyenes from the literature [91-93] {Cis 1,3,5 hexatriene (δ in PPM): δ 5.1 (4H), δ 5.9

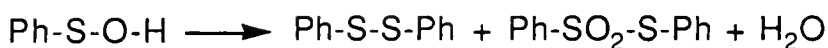
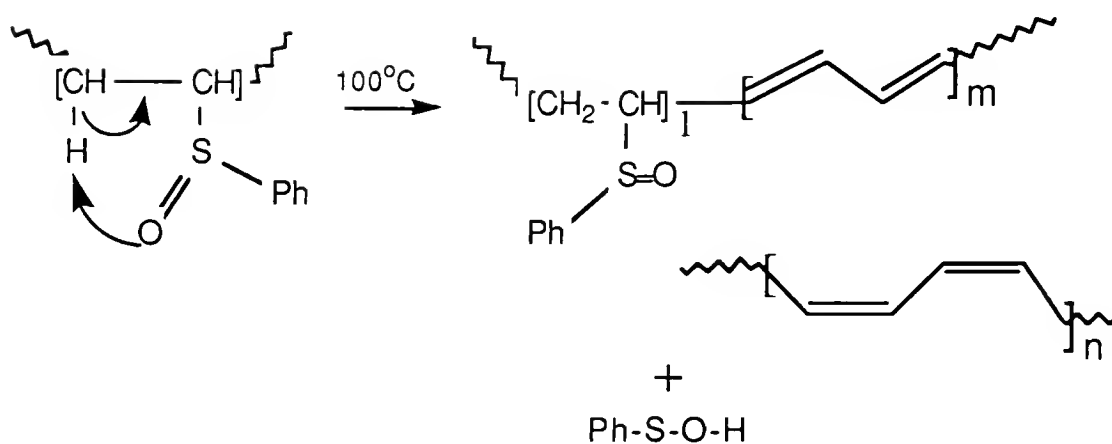


Figure 4-19. Sequence of events in the high temperature ^1H NMR studies of PPVS in CD_3COOD .

Table 4-8. Data from the high temperature 300 MHz ^1H NMR of PPVS in CD_3COOD .

Temperature $^\circ\text{C}$	Area of polyenes ^a	Area of PPVS methine ^b	% Polyenes
80	0.1745	0.8255	9.56
100	0.5561	0.8255	38.5
120	0.7021	0.2979	54.1
140	0.7311	0.2689	57.6

a. Normalized area of integration of the polyene absorptions at δ 5.7 PPM and δ 6.3 PPM.

b. Normalized area of integration of the PPVS methine absorption at δ 3.2 PPM.

δ 6.7 (2H). Trans 1,3,5 hexatriene (δ in PPM): δ 5.1 (4H), δ 6.2 (4H). (E,E)-Octa-1,3,5,7-tetraene (δ in PPM): δ 4.9-5.5 (4H), δ 6.3 (6H). (E,E,E)-Nona-1,3,5,7-tetraene (δ in PPM): δ 1.8 (3H), δ 4.9-6.0 (2H), δ 6.0-6.5 (7H). (E,E,E)-Deca-1,3,5,7,9-pentaene (δ in PPM): δ 5.0-5.3 (4H), δ 6.3 (8H)}.

Thus absorptions at δ 5.8 PPM and δ 6.3 PPM are reasonably attributable to cis and trans polyenes. Sharpening of peaks in the aromatic region is seen because of the formation low molecular weight elimination products as shown before. At 150°C all the peaks (except the aromatic absorptions of the eliminated products) disappear. At this stage (55% polyene, Table 4-8) the polyene linkages renders the polymer insoluble and it precipitates out.

Infrared (IR)

IR was used both for routine identification of homo- and copolymers as well as for the interpretation of the thermolysis process in PPVS. Unfortunately we could not derive much information of the polyacetylene absorptions from IR because of the high absorptivity of the residual sulfoxide groups in IR which overlaps with the =C-H bend absorption of polyacetylene.

A case in point is seen from Figure 4-20 which shows the change in IR of PPVS with temperature. The polymer was mixed with diamond powder and heated insitu under a flow of nitrogen. The spectra were scanned at various temperature intervals. At 30°C we see the characteristic IR of PPVS showing a strong absorption at 1041 cm^{-1} due to the S=O stretch of the sulfoxide group. Upon heating the polymer to 240°C we see the disappearance of the 1041 cm^{-1} absorption concurrent with the appearance of a strong absorption at 1143 cm^{-1} , medium absorptions at 1323 cm^{-1} , 1436 cm^{-1} , 1474 cm^{-1} and a weak absorption at 1575 cm^{-1} . The IR of PPVS at 240°C was identical to that of Ph-S-S-Ph and

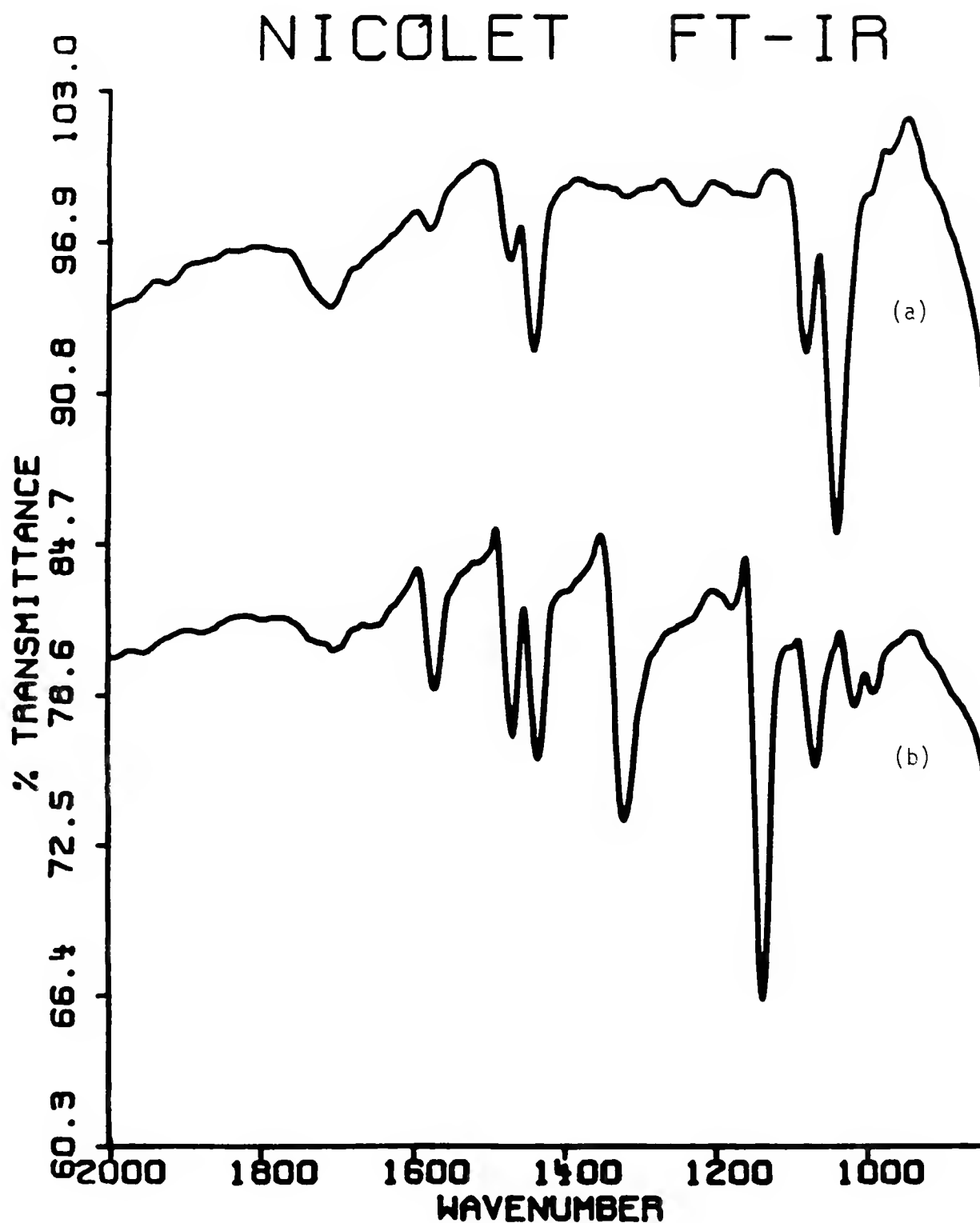


Figure 4-20. Change in the IR spectra of PPVS homopolymer with temperature: (a) 30°C and (b) 240°C, under nitrogen.

Ph-SO₂-S-Ph (Sadtlir). Thus the strong absorption at 1143 cm⁻¹ and 1323 cm⁻¹ are probably due to the O=S=O stretch and S-S stretch respectively of Ph-SO₂-S-Ph whereas the ones at 1436 cm⁻¹, 1474 cm⁻¹ and 1575 cm⁻¹ are due to Ph-S-S-Ph. Thus the eliminated products cloud the IR window and/or are left behind on the eliminated polymer giving no useful information on the cis or trans =CH absorptions.

In conclusion, the thermal elimination of phenyl sulfenic acid from PPVS homo- and copolymers was studied by TGA and pyrolysis-MS. The TGA of homopolymers typically show two degradation stages: one at lower temperature corresponding to elimination of phenyl sulfenic acid and one at higher temperatures corresponding to polyacetylene degradation. Pyrolysis-MS was used for elucidating the fate of phenyl sulfenic acid formed upon elimination. It was seen that the phenyl sulfenic acid, once formed, irreversibly dehydrates to form the anhydride benzenesulfinothioic acid, S-phenyl ester. This compound itself is not thermally stable and disproportionates rather readily to give diphenyl disulfide and benzenesulfonothioic acid, S-phenyl ester. There was a decided difference in the pyrolysis-MS at low and high temperatures. At low temperatures MS corresponding to the elimination of phenyl sulfenic acid and its further reaction was seen. At higher temperatures, however, formation of various aromatic hydrocarbons was seen typical of PA decomposition. XPS was used to monitor the elimination reaction with temperature. At high temperatures (>200°C) the characteristic S2p peak at 166 eV disappears indicating complete elimination of phenyl sulfenic acid. Proton NMR was also used to characterize the elimination process and shows formation of cis and trans polyenes at high temperatures (>100°C). A change in IR

spectra with temperature was observed but gave no useful information about the polyenes formed.

REFERENCES

- 1 M. Buese and T.E. Hogen-Esch, Macromolecules, **20**, 1509 (1987).
- 2 M. Buese, Ph.D. Dissertation, University of Florida (1982).
- 3 C.A. Kingsbury and D.J. Cram, J. Am. Chem. Soc., **82**, 1810 (1960).
- 4 R. Takinaga, H. Sugihara, K. Tanaka and A. Kaji, Synthesis, 299 (1975).
- 5 C. Walling and L. Bollyky, J. Org. Chem., **29**, 2699 (1964).
- 6 G. A. Koppel and M. D. Kinnick, J. Chem. Soc. Chem. Comm., 473 (1975).
- 7 J.L. Kice and J.D. Campbell, J. Org. Chem., **32**, 1631 (1967).
- 8 G. Tsuchihashi, S. Mitamura and K. Ogura, Tetrahedron Lett., **27**, 2469 (1973).
- 9 G. Tsuchihashi, S. Mitamura and K. Ogura, Tetrahedron Lett., **11**, 855 (1976).
- 10 L.A. Paquette, R.E. Moerck, B. Harirchian and P.D. Magnus, J. Am. Chem. Soc., **100**, 1597 (1978).
- 11 J.E. Frommer and R.R. Chance, Encycl. Polym. Sci. Eng., **5**, 462 (1986).
- 12 T. Ito, H. Shirakawa and S. Ikeda, J. Polym. Sci., Polym. Chem. Ed., **12**, 11 (1974).
- 13 R. Kaner and A. MacDiarmid, Scientific American, **258(2)**, 106 (1988).
- 14 N. Basescu, Z.X. Liu, D. Moses, A.J. Heeger, H. Narmann and N. Theophilou, Nature, **327**, 403 (1988).
- 15 C.S. Marvel, J.H. Sample and M.F. Roy, J. Am. Chem. Soc., **61**, 3241 (1939).
- 16 W.J. Feast, M.J. Taylor and J.N. Winter, Polymer, **28**, 593 (1987).

- 17 W.J. Feast and J.N. Winter, J. Chem. Soc., Chem. Commun., **202** (1985).
- 18 J. H. Edwards, W.J. Feast and D.C. Bott, Polymer, **25**, 395 (1984).
- 19 J. H. Edwards and W.J. Feast, Polymer, **21**, 595 (1980).
- 20 T. Swager, D. Dougherty and R. Grubbs, J. Am. Chem. Soc., **110**, 2973 (1988).
- 21 M. Aldissi, J. Chem. Soc., Chem. Commun., 1347 (1984).
- 22 M. Aldissi, Syn. Met., **13**, 87 (1986).
- 23 G.L. Baker and F.S. Bates, Macromolecules, **17**, 2619 (1984).
- 24 J.A. Stowell, A.J. Amass, M.S. Beevers and T.R. Farren, Makromol. Chem., **188**, 1635 (1987).
25. M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Wiley-Interscience, New York (1968).
26. M. Morton, "Anionic Polymerization, Principles and Practice," Academic Press, New York (1983).
- 27 M. Morton, R. Milkovich, D.B. McIntyre and L.J. Bradley, J. Polm. Sci.: Part A, **1**, 443 (1963).
- 28 R. Allen, T. Long and J. McGrath, "Advances in Polymer Synthesis," B. Culbertson and J. McGrath Eds., Plenum, New York, 347 (1985).
- 29 R. Allen, T. Long and J. McGrath, Polym. Bull., **15(2)**, 54(1986).
- 30 F. Schué and S. Bywater, Bull. Soc. Chim., **1**, 271 (1970).
- 31 J. Smid, J. Am. Chem. Soc., **87**, 655 (1965).
- 32 W.R. Sorenson and T.W. Campbell, "Preparative Methods of Polymer Chemistry," Interscience, New York (1961).
- 33 M. Doherty, Ph.D. Dissertation, University of Florida (1984).
- 34 W. Toreki, T.E. Hogen-Esch and G.B. Butler, Polym. Prepr., Am. Chem. Soc. (Div. Polym. Chem.), **27(1)**, 355 (1986).
- 35 T.E. Hogen-Esch and J. Smid, J. Am. Chem. Soc., **87**, 669 (1965).

- 36 T.E. Hogen-Esch and J. Smid, J. Am. Chem. Soc., **88**, 307 (1966).
- 37 T.E. Hogen-Esch, Ph.D. Dissertation, State University of Leiden, Netherlands (1967).
- 38 V.N. Ipatieff and B.S. Friedman, J. Am. Chem. Soc., **61**, 684 (1939).
- 39 J.H. Carter and F.W. Michelotti, Polym. Prepr., Am. Chem. Soc. (Div Polym. Chem.), **5**(2), 614 (1964).
- 40 W. Toreki, Ph.D. Dissertation, University of Florida (1988).
- 41 J.E. Mulvaney and R.A. Ottaviani, J. Polym. Sci., Part A-1, **8**, 2293 (1970).
- 42 J. Jacobus and K. Mislow, J. Am. Chem. Soc., **89**, 5228 (1967).
- 43 N. Kunieda, M. Kinoshita and M. Imoto, Polym. Lett., **9**, 241 (1971).
- 44 N. Kunieda, H. Wada and M. Kinoshita, Makromol. Chem., **172**, 237 (1973).
- 45 K. Andersen, S. Yeager and N.B. Peynircioglu, Tetrahedron Lett., **28**, 2485 (1970).
- 46 J.P. Lockard, C.W. Schroek and C.R. Johnson, Synthesis, 485 (1973).
- 47 T. Durst, M. LeBelle, R. Van den Elzen and K. Tin, Can. J. Chem., **52**, 761 (1974).
- 48 G. Solladie, Synthesis, 185 (1981).
- 49 R. Lett and A. Marquet, Tetrahedron Lett., **19**, 1579 (1975).
- 50 R. Lett, G. Chassaing and A. Marquet, J. Organometal. Chem., **111**, C17 (1976).
- 51 G. Chassaing and A. Marquet, Tetrahedron, **34**, 1399 (1978).
- 52 D. Rayner, A. Gordon and K. Mislow, J. Am. Chem. Soc., **90**, 4854 (1968).
- 53 E. Miller, D. Rayner, H. Thomas and K. Mislow, J. Am. Chem. Soc., **90**, 4861 (1968).

- 54 H. Kwart, T. George, R. Louw and W. Ultee, J. Am. Chem. Soc., **100**, 3927 (1978).
- 55 T. Wallace, J. Hofmann and A. Schriesheim, J. Am. Chem. Soc., **85**, 2739 (1963).
- 56 G.A. Russell and H.D. Becker, J. Am. Chem. Soc., **85**, 3406 (1963).
- 57 D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York (1965).
- 58 F.A. Bovey, F.P. Hood III, E.W. Anderson and L.C. Snyder, J. Am. Chem. Soc., **42**, 3900 (1965).
- 59 J.W. Dean, Polym. Lett., **8**, 677 (1970).
- 60 N. Grabowsky, Justus Liebigs Ann. Chem., **175**, 348 (1875).
- 61 A.C. Cope and D.L. Ross, J. Am. Chem. Soc., **83**, 3854 (1961).
- 62 H. Reich, I. Reich, J. Renga, J. Am. Chem. Soc., **95**, 5813 (1973).
- 63 B.M. Trost and A. Bridges, J. Org. Chem., **40**, 2014 (1975).
- 64 B.M. Trost and T.N. Salzmann, J. Am. Chem. Soc., **95**, 6840 (1975).
- 65 B.M. Trost, T.N. Salzmann and K. Hiroi, J. Am. Chem. Soc., **98**, 4887 (1976).
- 66 D. Emerson and T. Korniski, J. Org. Chem., **34**, 4115 (1969).
- 67 D.N. Jones, D.R. Hill, D.A. Lewton and C. Sheppard, J. Chem. Soc., Perkin I, 1574 (1977).
- 68 K. Matsumoto, T. Uchida and L.A. Paquette, Synthesis, 746 (1979).
- 69 B.M. Trost and K.K. Leung, Tetrahedron Lett., **48**, 4197 (1975).
- 70 J. Nokami, N. Kunieda and M. Kinoshita, Tetrahedron Lett., **33**, 2841 (1975).
- 71 E. Block and J. O'Connor, J. Am. Chem. Soc., **96**, 3921 (1974).
- 72 E. Block and J. O'Connor, J. Am. Chem. Soc., **96**, 3929 (1974).
- 73 P. Koch, E. Ciuffarin and A. Fava, J. Am. Chem. Soc., **92**, 5971 (1970).

- 74 J.R. Shelton and K.E. Davis, J. Am. Chem. Soc., **89**, 718 (1967).
- 75 J.L. Kice and J.P. Cleveland, J. Am. Chem. Soc., **95**, 104 (1973).
- 76 T.S. Chou, Tetrahedron Lett., **9**, 725 (1974).
- 77 E. Block, "Reactions of Organosulfur Compounds," Academic Press, New York (1978).
- 78 G. Montaudo, C. Puglisi, E. Scamporrino and D. Vitalini, J. Polym. Sci., Polym. Chem. Ed., **24**, 301 (1986).
- 79 A. Ballistreri, S. Foti, G. Montaudo and E. Scamporrino, J. Polym. Sci., Polym. Chem. Ed., **18**, 1147 (1980).
- 80 F. Will and D. McKee, J. Polym. Sci., Polym. Chem. Ed., **21**, 3479 (1983).
- 81 J. Chien, P. Uden, J. Fan, J. Polym. Sci., Polym. Chem. Ed., **20**, 2159 (1982).
- 82 E. Turi, "Thermal Characterization of Polymeric Materials," Academic Press, New York (1981).
- 83 I. Lüderwald and O. Vogl, Makromol. Chem., **180**, 2295 (1979).
- 84 L. Bark and N. Allen, "Analysis of Polymer Systems," Applied Science, London (1982).
- 85 C. Brown, P. Kovacic, C. Wilkie, R. Cody, R. Hein and J. Kinsinger, Synthetic Metals, **15**, 265 (1986).
- 86 H. Schulten and R. Lattimer, Mass Spectrometry Reviews, **3**, 231 (1984).
- 87 W. Riggs and R. Beimer, Chemtech, 652 (1975).
- 88 J.D. Andrade, "Surface and Interfacial Aspects of Biomedical Polymers," Plenum Press, New York (1981).
- 89 C. Wagner, W. Riggs, L. Davis, J. Moulder and G. Mullenberd, "Handbook of X-ray Photoelectron Spectroscopy," P.E. Corporation Publication, Minnesota (1979).
- 90 D. Briggs, D. Rance, C. Kendall and A. Blythe, Polymer, **21**, 895 (1980).

- 91 P. Albriksen and R. Harris, Acta Chem. Scand., **27(6)**, 1875 (1973).
- 92 C. Spangler and D. Little, J. Chem. Soc., Perkin Trans. I, **10**, 2379 (1982).
- 93 E. Block, M. Aslam, V. Eswarakrishnan, K. Gebreyes, J. Hutchinson, R. Iyer, J. Laffitte and A. Wall, J. Am. Chem. Soc., **108**, 4568 (1986).

BIOGRAPHICAL SKETCH

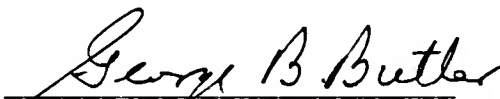
Rustom Sam Kanga was born in Bombay, India, with twelve fingers. At the time of securing his doctorate he was left with eleven.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



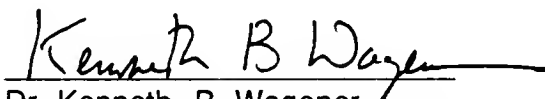
Dr. Thieo E. Hogen-Esch, Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Dr. George B. Butler
Professor Emeritus of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



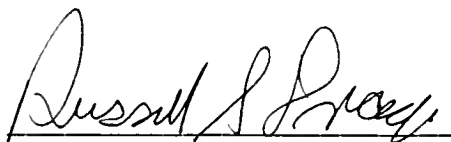
Dr. Kenneth B. Wagener
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Dr. Merle A. Battiste
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Dr. Russell S. Drago
Graduate Research Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Dr. Christopher D. Batich
Associate Professor of Materials Science
and Engineering

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 1988

Dean, Graduate School

UNIVERSITY OF FLORIDA



3 1262 08556 7690